SURFACE CHARGE PROPERTIES OF TROPICAL SOILS AND THEIR INFLUENCE ON Cd AND Pb SORPTION

By

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Abstract of Dissertation Presented to the Graduate School
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SURFACE CHARGE PROPERTIES OF TROPICAL SOILS
AND THEIR INFLUENCE ON Cd AND Pb SORPTION

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Reactions of heavy metals with soil are important in determining metal fates in the environment. Important factors affecting heavy metal retention by soils are pH, ionic strength (I), and surface charge, as well as chemical characteristics of heavy metals. The objectives of this study were to (1) measure the surface charge and points of zero charge of surface horizons from two highly weathered soils from Puerto Rico, an Oxisol and Ultisol, as well as mineral standard kaolinite and synthetic goethite using three methods – a) potentiometric titration, b) ion adsorption, and c) electroacoustic mobility; (2) determine sorption characteristics of Cd and Pb in the Oxisol, Ultisol, and a Mollisol (also from Puerto Rico) as a function of varying metal concentration, pH, I, and surface charge; (3) evaluate the ability of the three soils to retain Cd and Pb when the metals were added to these soils in a sequential reaction scheme; and to (4) measure cation selectivity and surface heterogeneity of K/Ca and K/Pb systems in the Oxisol and Ultisol using calculated Gaines-Thomas selectivity coefficients (K_{GT}) coupled with enthalpy

change (ΔH) data obtained using a flow calorimeter. The points of zero charge determined in this study for kaolinite and goethite were comparable with those reported in the literature. The points of zero charge obtained for the Oxisol and Ultisol were consistent with these soils' chemical and mineralogical properties. All soils sorbed Pb in preference to Cd regardless of initial metal concentration, pH, *I*, surface charge, or sequence of metal addition. Sorption appeared to be more dependent on metal type than soil composition and Pb was much less exchangeable than Cd. The K_{GT} and surface heterogeneity data demonstrated the importance of soil components in the exchange reactions involving K/Ca and K/Pb systems in the Oxisol and Ultisol. The Oxisol was composed of homogeneous adsorption sites while the Ultisol was made up of sites exhibiting surface heterogeneity. Therefore, retention of Cd and Pb by tropical soils is dependent on both metal type and soil composition. Lead poses less of a threat to groundwater systems than Cd due to Pb's lower mobility and bioavailability.

CHAPTER 1
INTRODUCTION

The study of heavy metal contamination in soils has received much attention in the last several decades due to the potential deleterious effects of these elements to plants and animals. As a result, regulators around the world have implemented much legislation aimed at curbing the build-up of heavy metals in the environment (Manahan, 1990). Cadmium (Cd) and lead (Pb) are two heavy metals which have been extensively researched in the developed, generally temperate and sub-tropical, regions of the globe due to their harmful effects on humans and widespread use in industry, agriculture, and urban activities (Adriano, 1986; Forstner, 1995; Nriagu, 1998).

In the tropics, however, relatively few studies have been conducted on Cd and Pb contamination in soils. This is partly due to the fact that a majority of countries in the tropics may be considered developing nations. Thus, resource allocation to environmental contamination by heavy metals in these areas is much lower than in most of their temperate region counterparts. Furthermore, legislation to protect against build-up of potential environmental toxins such as Cd and Pb is generally weak with no legal accountability (Moreira, 1996).

The characteristics of many tropical soils may further aggravate the problem of heavy metal contamination in these regions. Unlike most temperate region soils, highly weathered tropical soils have very low negative surface charge or retention capacity of cationic nutrients or contaminants. Under certain condition, they may exhibit a net

positive surface charge, thus, repelling cations. Cations, such as Cd and Pb, therefore, are more likely to be mobile in these highly weathered soils than in temperate region soils. This potentially has great impact on soil and groundwater quality and human health in these areas.

The main objectives of this study were to investigate surface charge development in highly weathered tropical soils and ascertain how this parameter affected the sorption of Cd and Pb on tropical soil surfaces. The first two studies (Chapters 3 and 4) examined the measurement of soil surface charge and, established how soil surface charge and factors such as pH and ionic strength affected Cd and Pb sorption. The latter investigations (Chapters 5 and 6) were geared toward understanding how Cd, Pb, calcium (Ca), and potassium (K) interact with highly weathered soil surfaces when applied sequentially and together. Also, the thermodynamics, in particular the enthalpy change, associated with K/Ca and K/Pb exchange and sorption, was studied using flow calorimetry. The last chapter presents a synthesis of the important conclusions and considerations learned from each of these experiments.

CHAPTER 2
LITERATURE REVIEW

Heavy Metal Contamination in Soils

Unlimited growth of living organisms is controlled via two mechanisms. Nutrients may become limited and/or waste products increase within the growth medium producing toxicity. The increasing consumption, production, and exploitation of the earth's raw materials (e.g. fossil fuels and minerals), coupled with the exponential growth of the world's population over the past 200 years, have resulted in environmental build-up of waste products (Adriano, 1986; Purves, 1977). The major sinks for these materials include the earth's waters, soils, and atmosphere.

The accumulation of these wastes has resulted in contamination and pollution of many natural ecosystems (Brendecke and Pepper, 1996; de Haan and van Riemsdijk, 1985). Although used interchangeably, contamination and pollution are two different terms. Contamination refers to the concentration of a substance in the environment at greater than natural levels which may yield undesirable effects. Pollution is the introduction of materials or energy into the environment likely to cause hazards to human health, negative impacts on natural resources and ecological systems, injury to structures, and obstruction to acceptable uses of the environment (Alloway, 1990a). Contaminants come from a myriad of sources and exhibit much heterogeneity. Based upon their

chemical properties, however, they may be grouped into organic compounds, inorganic materials, radioactive substances, or a combination of these.

Beginning in the 1970s, widespread public concern over the environmental hazards posed by the above materials prompted the worldwide implementation of much legislation. For example, the United States Congress has passed the Federal Water Pollution Control Acts; the Federal Insecticide, Fungicide, and Rodenticide Act of 1972; the Toxic Substances Control Act of 1976; the Superfund Amendments and Reauthorization Act of 1986; the Hazardous and Solid Wastes Amendments of 1984; and the Ocean Dumping Ban Act of 1992 each of which was aimed at controlling environmental pollution (Manahan, 1990; U.S. EPA, 1991).

Many countries have numerous contaminated sites. A 1988 survey of five countries in the European Community shows there were about 8,900 contaminated industrial sites posing environmental health problems. These sites comprise nearly 0.2 % of the total land areas in these countries. In Denmark, Germany, and The Netherlands, over 14,000 contaminated or possibly contaminated sites exist. Moreover, in the developing world, due to the lack of infrastructure associated with industrialization processes, environmental contamination has become a more severe problem. In the United States, the National Priority List (Superfund Sites) (U.S. EPA, 1986) had >1000 sites containing environmental or health risks. Around 40% of these areas reported heavy metal problems (Forstner, 1995).

The main elements listed as being problematic at these Superfund Sites were Pb, Cr, As, and Cd (50 sites each) and Cu, Zn, Hg, and Ni (20 sites each). The predominant industrial activities responsible for these metal problems were metal plating, chemical

waste dumping/landfilling, mining and smelting, battery recycling, CCA (Cu, Cr, As) wood treatment, oil and solvent recycling, and nuclear processing industries (Forstner, 1995) (Table 2-1).

Table 2-1. Partial listing of heavy metals at Superfund Sites.

# of sites	Type of industry	Heavy metals of concern							
154	Landfill/chemical waste dump	Pb	Cr	As	Cd	Ni	Zn	Ba	Mn
43	Metal finishing/plating/electronics	Pb	Cr	As	Cd	Ni	Zn	Fe	Cu
35	Chemical/pharmaceutical	Pb	Cr	As	Cd			Hg	Cu
28	Mining/ore processing/smelting	Pb	Cr	As	Cd	Ag	Zn	Fe	Cu
21	Federal (DOD, DOE)	Pb	Cr	As	Cd	Ni	Zn	Hg	
19	Battery recycling	Pb			Cd	Ni	Zn		Cu
18	CCA wood treatment		Cr	As					Cu
16	Oil and solvent recycling	Pb	Cr	As			Zn		
13	Nuclear processing/equipment						Ra	Th	U
5	Pesticide			As					
5	Vehicle drum cleaning			As					
3	Paint	Pb	Cr		Cd			Hg	
29	Other	Pb	Cr	As				Hg	

Adapted from Forstner, 1995.

Recently, much focus has been placed on the study and fate of inorganic contaminants, particularly heavy metals, in soils (Chen and Ma, 1998; Filius et al., 1998; Hanafi and Sjiaola, 1998; Hyun et al., 1998; Krebs et al., 1998; McLaren et al., 1998; Wilcke et al., 1998a). Heavy metals may include those elements occurring in natural systems in low concentrations (i.e. < 100 -1000 ppm, e.g. Cd, Cu, Ni, Pb, and Zn). This definition can be broadened to include those elements, present in the biosphere, other than the eight most abundant rock-forming elements (O, Si, Al, Fe, Ca, Na, K, and Mg) (Adriano, 1986).

Heavy metals are natural constituents of soils and rocks (Table 2-2); however, as a result of industrialization and mining activities over the past 200 years, concentration, deposition, and dispersion of these materials in the environment have increased (Davies, 1992; Forstner, 1995). Worldwide, this has resulted in groundwater contamination as well as soil deterioration (Davies, 1992; Forstner, 1995; Purves, 1977).

Table 2-2. Average heavy metal and trace element concentrations (ppm) in uncontaminated surface soil, various soil-forming rocks, and natural materials.

		Igneous rocks			Sedimentary rocks		
Element	Soil	Ultra-mafic	Basaltic	Granitic	Shales and clays	Black shales	Sandstones
As	6	3	2	2	10	-	2
Ba	500	1	300	700	700	300	20
Be	0.3	-	1	3	3	-	-
Cd	0.35	0.05	0.2	0.15	1.4	1.0	0.05
Co	8	150	50	5	20	10	0.3
Cr	70	1,800	220	20	120	100	35
Cu	30	15	91	15	50	70	2
F	200	-	360	870	800	-	180
Hg	0.06	0.1	0.05	0.06	0.09	0.5	0.05
Mo	1.2	0.3	1.5	1.4	2.5	10	0.2
Ni	50	2,000	140	8	68	50	2
Pb	35	-	18	30	50	150	31
Se	0.4	0.05	0.05	0.05	0.6	-	0.05
V	90	40	250	60	130	150	20
Zn	90	40	110	40	90	100	16

Adapted from Adriano, 1986.

Important heavy metals posing threats to soil quality and human health are Cd and Pb as they are widely used for a variety of industrial, urban, and agricultural applications (Adriano, 1986; Angelone and Bini, 1992; Forstner, 1995; Kabata-Pendias and Pendias, 1992). Industrial and urban sources of soil contamination include mining and smelting,

coal residues, municipal refuse, and auto emissions. Agricultural origins include commercial fertilizers, limes, pesticides, and animal wastes. Furthermore, biosolids (industrial and urban sources) have recently received much study as a soil amendment and are a possible source of heavy metals in soils. Annual production rates for metal-containing solid and semi-solid wastes in the USA during the years 1970-1974 from industrial, municipal, and agricultural sources were 2035 x 10^6, 138 x 10^6, and 687 x 10^6 tons per year, respectively (Adriano, 1986).

Toxicities of Cd and Pb to Humans

Toxic substances are materials which, above a certain level of exposure or dose, have harmful effects on organs, tissues, and biological processes. The U.S. EPA has developed human exposure limits for Cd and Pb as these elements can be toxic to humans at high levels (Manahan, 1990). The maximum contamination levels (MCL) in drinking water for Cd and Pb are 5 and 15 $\mu g\ L^{-1}$ (U.S. EPA, 1994). Table 2-3 shows the soil cleanup target levels (SCTL) required by the U.S. EPA and Florida Department of Environmental Protection for these elements.

Table 2-3. U.S. EPA MCLs and Florida SCTLs for Cd and Pb in soil (mg kg^{-1}).

		Florida‡	
Contaminant	U.S. EPA†	Residential	Industrial
Cd	0.005	75	1300
Pb	NA	500	920

†Adapted from U.S. EPA, 1996.
‡Adapted from Tonner-Navarro et al., 1998.

A brief description of the exposure and modes of uptake for the above elements as well as their potential adverse effects to human health follows.

Cadmium

The main pathways of Cd exposure to humans are through inhalation, ingestion, and to a limited extent dermal absorption. Dusts and aerosols containing Cd are readily absorbed in the lungs with ~ 30 to 50 % absorption rate. Plants can easily take up Cd, especially under low pH, from the soil and aquatic organisms may do the same from water. Cadmium can then bioaccumulate in the food chain and can be present in relatively high concentrations in plants and animals. Moreover, upon entering the body, Cd is retained such that low doses can build-up to high levels when exposure takes place over an extended period (Hrudey et al., 1995; U.S. EPA, 1992).

Ingestion of high doses of Cd leads to stomach irritation, vomiting, and diarrhea while inhalation of large quantities causes severe lung irritation. People exposed to low levels of Cd over an extended period of time may incur kidney damage as well as lung, bone, cardiovascular system, liver, and reproductive system damage. This can result in lung disease, hypertension, Itai-Itai disease, lung cancer, and renal problems (Hrudey et al., 1995; U.S. EPA, 1992).

Lead

Lead may be ingested, inhaled, or absorbed by human skin. Nearly all the Pb entering the body via inhalation or dermal contact moves to the blood. In young children, Pb from ingestion of food or soil containing Pb moves readily to the blood and other parts

of the body. In contrast, only a small fraction of the ingested Pb enters the blood in adults. However, once Pb makes it to the bloodstream, most is stored in bones and teeth and accumulates with age (Hrudey et al., 1995; U.S. EPA, 1992).

Lead may have adverse effects on people of all ages. However, its toxicity to children is most significant. Toxicity occurs in children at much lower levels as they absorb Pb more readily. Low levels of Pb exposure have led to decreased IQ scores, retardation of physical growth, hearing problems, impaired learning, and decreased attention and classroom performance. In individuals of all ages, Pb may cause anemia, kidney disease, brain damage, impaired function of the peripheral nervous system, high blood pressure, reproductive abnormalities, developmental defects, abnormal vitamin D metabolism, and in some situations death (Hrudey et al., 1995; U.S. EPA, 1992).

Speciation and Bioavailability of Cd and Pb in Soils

Via a variety of pathways, environmental contaminants are transported and may become available to organisms for uptake. Bioavailability describes the rate and extent a chemical is released from a certain media (e.g. soil, water, etc.) into the environment and is available to living receptors (e.g. plants and animals) through a complete exposure pathway (Hrudey et al., 1995).

A contaminant's concentration, though important, is of secondary significance when ascertaining bioavailability. Speciation, knowledge of the chemical and physical associations which a material undergoes, is the main determiner of a contaminant's distribution, mobility, and biological availability in the environment. Therefore, changes in environmental conditions such as pH, redox potential, availability of both organic and

inorganic ligands, adsorbing particle surfaces, and colloidal matter significantly influence the forms and reactions of metal-laden materials in the environment (Ure and Davidson, 1995).

The speciation and plant bioavailability of Cd and Pb are contingent upon their interactions within certain soil compartments. The various fates and equilibria existing between the above metals in the soil solution are uptake and release by plants, precipitation and mineral formation, exchange and adsorption by mineral constituents, exchange with gaseous phases, fixation and release by microbes, exchange and adsorption by organic matter, and organic matter formation and decomposition (Kabata-Pendias and Pendias, 1992).

In order to achieve appropriate representations of how Cd and Pb exist in soils, it is first necessary to delineate the most common soil fractions and how the above metals may be affiliated therein. These elements may exist in one or more of the following phases: water soluble – in the soil solution/water filled pore space as ions or complexes; exchangeable – adsorbed electrostatically by negatively charged exchange sites on clays, organic matter, and hydrous oxides; carbonate bound – precipitated with carbonate in soils high in $CaCO_3$, HCO_3^-, and alkaline pH; reducible – adsorbed/co-precipitated with oxides, hydroxides, and hydrous oxides of Fe, Mn, and to some extent Al; organic matter bound – complexed/chelated/bound with various organic matter fractions ranging in stability and mobility; and residual – fixed within the lattices of minerals. The phases most readily available to plants include the solution and exchangeable fractions with metals decreasing in plant availability continuing down the association scheme. Metals in the residual phase are generally considered unavailable (Adriano, 1986; Alloway,

1990b; Kabata-Pendias and Pendias, 1992; Ritchie and Sposito, 1995; Srivastava and Gupta, 1996; Tessier et al., 1979).

The following discussion will give a brief account of the important species of Cd and Pb (besides those listed in Table 2-1) occurring in normal, uncontaminated soils (Table 2-4). In contaminated soils, the speciation of each metal will be similar, however, equilibrium will be shifted toward formation of products with increasing reactant or metal concentration. This will be followed by a consideration of a few very important environmental factors – pH and adsorption onto organic and inorganic materials – affecting their availability to plants.

Table 2-4. Oxidation states and average concentrations (mol L^{-1}) of Cd and Pb in uncontaminated soil (Lindsay, 1979).

Metal	Oxidation states†	Concentration
Cd	0, **+2**	5.3×10^{-7}
Pb	0, **+2**, +4	9.4×10^{-5}

†Most important oxidation state in soils denoted with boldface type.

Cadmium

The most stable oxidation state for Cd in soil is +2. At pH values above about 7.5, the activity of Cd^{2+} may be reduced by formation of the minerals $Cd_3(PO_4)_2$ and $CdCO_3$ (octavite) while at pH above 9, the formation of $CdSiO_4$ and $Cd(OH)_2$ is possible but unlikely. Santillan-Medrano and Jurinak (1975) found, at relatively high Cd concentrations, the precipitation of $Cd_3(PO_4)_2$ and/or $CdCO_3$ limited Cd solubility in an alkaline soil. Under most soil conditions (pH 3.5 - 9 and Eh 350 - 700 mV), the predominant ionic form of cadmium is Cd^{2+}; however, above pH 7.5, $CdOH^+$ and

$CdHCO_3^+$ may contribute significantly to the amount of cadmium in solution. Furthermore, at pH near 8 and high NH_4^+ activities (> 1 *M*) (possible in the immediate vicinity of some NH_4^+ fertilizers), $CdNH_3^{2+}$ to $Cd(NH_3)_4^{2+}$ may temporarily solubilize Cd. Cadmium may also exist as $CdSO_4$ at pH above and below 7. At Cl^- activities above 10^{-2} *M*, $CdCl^+$ species may become important in the soil solution (Lindsay, 1979). Bingham et al. (1984) found $CaCl_2$ additions increased the amount of Cd uptake by Swiss chard leaves while Doner (1978) demonstrated Cd mobility through a soil column increased in the presence of NaCl. Cadmium may also be associated with organic materials at normal soil pH values (3.5 - 9) (Alloway, 1990b; Kabata-Pendias and Pendias, 1992; Srivastava and Gupta, 1996).

Lead

In soils, lead may exist as Pb^{2+} and under highly oxidized conditions as Pb^{4+}; however, it generally has the former oxidation state. Under alkaline conditions and relatively high Pb^{2+} concentrations (> 10^{-3} *M*), its solubility may be limited by formation of PbO. At Pb^{2+} concentrations of 10^{-8} *M* and alkaline conditions, $Pb(OH)_2$, $PbCO_3$, and $Pb_3(CO_3)_2(OH)_2$ may be stable with increasing formation of $PbCO_3$ at higher partial pressure of CO_2. Furthermore, over a wide pH range and in the presence of 10^{-3} *M* SO_4^{2-}, $PbSO_4$ limits Pb^{2+} solubility. At pH less than 6, $PbSO_4$ is the most stable mineral of those listed above while at higher pHs, $PbCO_3$ is most stable (Lindsay, 1979). Phospho-lead minerals can be very important in lowering Pb^{2+} solubility. Under normal soil conditions (pH 3.5 - 9 and Eh 350 - 700 mV), $Pb_5(PO_4)_3F$ (fluoropyromorphite) $Pb_5(PO_4)_3OH$ (pyromorphite), $Pb_3(PO_4)_2$, and $Pb_5(PO_4)_3Cl$ (chloropyromorphite) are the

main minerals decreasing Pb^{2+} activity. Chloropyromorphite has the ability to control Pb^{2+} solubility in pH ranges found in most soils. However, at pH below 6, Pb^{2+} solubility increases as PO_4^{3-} activity is depressed by Fe^{3+} and Al^{3+}. At pH less than 4, $PbSO_4$ is more stable than chloropyromorphite (Lindsay, 1979). Ma (1996) and Ma et al. (1995, 1994a, b) have shown how the phosphate minerals decrease the solubility of Pb^{2+} under a myriad of conditions.

Lead occurs ionically in soils in a variety of forms. Below pH 8, only Pb^{2+} and $PbOH^+$ are present in significant concentrations in the soil solution. Above pH 9, $Pb(OH)_2$, $Pb(OH)_3^-$, and $Pb(OH)_4^{2-}$ can slightly contribute to Pb species in soils. Moreover, at halide activities more than 10^{-4} *M*, $PbCl^-$ and PbF^- may form. Lead complexes of $PbNO_3^+$ (NO_3^- activity > 10^{-3} *M*) and $PbHPO_4$ (pH > 7) are possible but not of great importance. Lead associations with organic matter also affect its solubility (Kabata-Pendias and Pendias, 1992; Lindsay, 1979; Srivastava, 1996).

Cd and Pb Contamination in the Tropics

Many studies have evaluated the concentrations, mobilities, and partitioning of trace metals in temperate soils (Barbarick et al., 1998; Chang et al., 1984; Gong and Donahoe, 1997a; Jang et al., 1998; Johnson and Petras, 1998; Jordan and LeChevalier, 1975). However, relatively few experiments have been conducted using tropical soils (Hanafi and Sjiaola, 1998; Hue and Ranjith, 1993; Naidu et al., 1997; Wilcke et al., 1998a). This has resulted in a large disparity between what is known about heavy metal contamination in temperate region soils compared to their tropical counterparts.

The problem of environmental contamination in the tropics is augmented when bearing in mind the majority of nations in the tropics may be considered developing nations. In many situations, to foster economic growth and development, foreign investment becomes essential. In these efforts to improve the economy, sacrifices are made in national policy and protective law to attract new investment. This can and has led to environmental contamination, nonexistent legal accountability for industry, weak or nonexistent protective laws relating to environmental and human health, and widespread soil, water, and air contamination (Moreira, 1996).

Further aggravating this problem of environmental deterioration in tropical regions, especially related to soils, are the properties exhibited by soil colloids in these regions. Whereas temperate region soils are composed of clays with mostly permanent negative charge, tropical soils are predominantly made up of variable-charged or pH-dependent charged materials. Therefore, under certain conditions, tropical soil colloids can have a very low negative surface charge while exhibiting a net positive charge (Keng and Uehara, 1974; Mekaru and Uehara, 1972; Naidu et al., 1997; Sanchez, 1976; Uehara and Gillman, 1981; van Raij and Peech, 1972). Many heavy metals of concern, particularly Cd and Pb, exist as cations in soil solution. They, therefore, exhibit a greater likelihood of mobilization in tropical soils than if they were present in soils with permanent negative surface charge (Hanafi and Sjiaola, 1998; Hue and Ranjith, 1993; Naidu et al., 1997; Wilcke et al., 1998a).

Extent of the Tropics and Tropical Soils

The classic definition of the tropics includes areas lying between the Tropic of Cancer (23.5° N latitude) and the Tropic of Capricorn (23.5° S latitude). This definition can be expanded to include any areas having hyper and isohyperthermic temperature regimes or a mean annual temperature of 22° C or greater (Soil Survey Staff, 1994). The soils in these regions makeup 38 % of the earth's land surface and form under a wide range of climates and rainfall patterns. Therefore, Aridisols can exist where rainfall is minimal while highly weathered Oxisols and Ultisols can dominate in locations where precipitation can reach 10,000 mm/yr in the tropics.

In many cases precipitation exceeds evapotranspiration in these areas. This, along with high mean annual temperature and heavy rainfall, causes intense soil weathering and leaching with buildup of kaolinitic and oxidic type minerals in the clay fraction. A majority (58 %) of the tropical landmass is composed of highly-weathered and variable-charge soils – Oxisols, Andisols, Ultisols, and acid Alfisols. Oxisols and Ultisols, which will be studied in this investigation, comprise about 34 % of tropical soils (Sanchez, 1976; Uehara and Gillman, 1981).

Surface Charge Origination in Tropical Soils

Soil minerals can be separated into two general groups with respect to the origin of their surface charge. The first group is composed of minerals predominantly found in the world's temperate regions. These minerals mostly possess a constant negative surface charge as a result of isomorphous substitution within their crystal lattices. The second

assemblage is made up of constant surface potential minerals that obtain their surface charge via adsorption of ions onto their surfaces. Net surface charge is resolved by those ions adsorbed in excess (potential determining ions) (Naidu et al., 1997; Sanchez, 1976; Uehara and Gillman, 1981).

Though a single mineral may have both types of surface charge, the dominance of origination of surface charge, exhibited in a group of minerals, via isomorphous substitution (i.e. constant surface charge) or potential determining ions (i.e. constant surface potential) can be evaluated. For example, derivation of surface charge in temperate region soils such as Mollisols and Vertisols, which contain clays predominantly made up of smectite and vermiculite, is almost entirely a result of isomorphous substitution. On the other hand, the highly weathered soils of the tropics including Oxisols and Ultisols, possessing clay fractions mainly composed of iron and aluminum oxides and hydroxides, obtain surface charge via adsorption of potential determining ions (Sanchez, 1976; Uehara and Gillman, 1981).

Minerals with constant surface potential get their surface charge as a result of sorption and desorption reactions with the potential determining ions H^+ and OH^- (Atkinson et al., 1967; Parks and de Bruyn, 1961; Sanchez, 1976; Uehara and Gillman, 1981; van Raij and Peech, 1972; Yopps and Fuerstenau, 1964). For example, in the case of the iron oxide, hematite, which has a hydroxylated surface, the activities of H^+ and OH^- in the soil solution (pH) will determine the surface charge of the mineral via sorption/desorption reactions (Fig. 2-1).

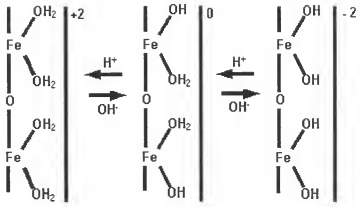

Figure 2-1. Hydroxylated surface charge variation as a function of potential determining ions H^+ and OH^- (Uehara and Gillman, 1981).

The figure shows three potential charge systems, suggesting a wide range of cation and anion exchange capacities. In an acid medium, the soil will sorb protons (H^+) and have a net positive charge (anion exchange capacity, AEC). On the other hand, in an alkaline environment, OH^- groups will deprotonate the hematite surface causing the mineral to possess a net negative charge (cation exchange capacity, CEC). Between these two charge systems is the isoelectric point or point where the surface charge is essentially zero (point of zero charge, PZC) (Boekhold et al., 1993; Naidu et al., 1994; Schofield, 1949; Uehara and Gillman, 1981).

The relationship between the potential determining ions, H^+ and OH^-, and surface charge may be further explained by the Gouy-Chapman Theory of the double layer. For colloids with constant surface potential, the equation looks like the following (Eq. 2-1) (Keng and Uehara, 1974; Naidu et al., 1997; Sanchez, 1976; Uehara and Gillman, 1981):

$$\sigma = [2\eta\varepsilon kT/\pi]^{1/2} \sinh 1.15\ z(pH_o - pH) \qquad [2\text{-}1]$$

σ = surface charge density ($cmol_c/kg$ soil)
η = counterion concentration in the equilibrium solution
ε = dielectric constant of the medium
k = Boltzmann constant
T = absolute temperature
sinh = hyperbolic sine
z = valence of counterion
pH_o = soil pH at the point of zero charge
pH = soil pH

Equation 2-1 demonstrates that soil pH directly impacts both the sign and magnitude of colloidal surface charge and the CEC and AEC. For example, if $pH_0 > pH$, then the soil colloids will have a net positive charge and exhibit AEC. At the other extreme, if $pH_0 <$ pH, then the soil colloids will have a net negative charge demonstrating CEC. If $pH_0 =$ pH, the soil colloids will have no charge exhibiting minimal electrostatic activity. Therefore, cation exchange, as well as the adsorption and leachability of ionic metals in soil, depends on the soil pH relative to the point of zero charge (Keng and Uehara, 1974; Naidu et al., 1997; Sanchez, 1976; Uehara and Gillman, 1981; van Raij and Peech, 1972).

Relatively pure iron and aluminum oxides, the predominant constituents in tropical soils, possess points of zero charge between pH 7 and 9 depending on their composition and degree of crystallinity (Parks and de Bruyn, 1961; Yopps and Fuerstenau, 1964). Organic matter and silica, on the other hand, have low points of zero charge and can increase CEC of soils with variable charge. In some cases, relatively small proportions (5 %) of iron and aluminum oxides have resulted in high points of zero charge (pH 6) as these materials can coat siliceous particles (Uehara and Gillman, 1981). Therefore, ways to increase negative surface charge (CEC) and decrease the point of zero

charge are important for heavy metal sorption and retention of cationic nutrients for agriculture.

Summary

The aim of this study was to evaluate the nature of heavy metal contamination as related to colloidal surface charge in an Oxisol, Ultisol, and Mollisol sampled from Puerto Rico. More specifically, the assumption that Cd and Pb availability, via sorption reactions, would be affected through a variety of treatments, was assessed.

CHAPTER 3
POINT OF ZERO CHARGE DETERMINATION IN SOILS AND MINERALS

Introduction

Several methods have been proposed for determination of the point of zero charge in soils and other materials dominated by variable surface-charge colloids. In soils, researchers have generally relied on potentiometric titration, which assesses changes in surface potential with changes in the activities of H^+ and OH^-, to determine the point of zero salt effect (PZSE) or point of zero net proton charge (PZNPC). They have also used non-specific ion adsorption, which measures changes in the electrostatic adsorption of a cation and anion with changes in the activities of H^+ and OH^-, to find the point of zero net charge (PZNC) (Marcano-Martinez and McBride, 1989; Parker et al., 1979; Parks and de Bruyn, 1961; Schofield, 1949; van Raij and Peech, 1972). Some researchers have proposed methods based on the mobility of charged particles in an electrical field (Findlay et al., 1996; O'Brien and Rowlands, 1993; Yopps and Fuerstenau, 1964). However, most of the research has focused on the use of these techniques for charge determination of pure mineral specimens (e.g. kaolinite, gibbsite, etc.) and not whole soils. The heterogeneous nature of soils in terms of particle size and extreme variety in types of charged particles makes detection of mobility difficult in these complex systems.

According to Barrow (1987) and Sposito (1989), the net total particle charge (σ_P) of a soil may be defined as follows:

$$\sigma_P = \sigma_O + \sigma_H + \sigma_{IS} + \sigma_{OS} \quad [3\text{-}1]$$

where σ_O refers to surface charge development arising from isomorphous substitution during mineral formation and is responsible for the permanent negative charge of many temperate-region soils. The net proton charge, σ_H, describes surface charge from adsorption of the potential-determining ions H^+ and OH^-. When ions, other than H^+ and OH^-, take part in coordination reactions with surfaces, inner-sphere surface complexes form with the ensuing surface charge deemed inner-sphere complex charge (σ_{IS}). Alternately, when ions other than H^+ and OH^- are adsorbed electrostatically and bound into outer-sphere surface complexes, which is inside the plane of shear – generally defined as the interface between the Stern and diffuse layers, outer-sphere complex charge (σ_{OS}) develops.

In any system composed of charged particles, the net total particle charge (σ_P) is balanced by ions of opposite charge in a diffuse layer (σ_D) surrounding the particle.

$$\sigma_P + \sigma_D = 0 \quad [3\text{-}2]$$

Therefore, the various points of zero charge of reversible interfaces may be defined as the pH values where one or more of the surface charge components defined in Eq. (3-1) is zero (Barrow, 1987; Lewis-Russ, 1991; Sposito, 1989).

$$\sigma_H = 0 = \text{PZNPC} \quad [3\text{-}3]$$
$$\sigma_{IS} + \sigma_{OS} + \sigma_D = 0 = \text{PZNC} \quad [3\text{-}4]$$
$$\sigma_P = 0 = \text{PZC} \quad [3\text{-}5]$$

The PZSE, on the other hand, corresponds to the pH where σ_H does not change with changes in I (Parker et al., 1979).

$$(\delta\sigma_H/\delta I)_T = 0 = \text{PZSE} \quad [3\text{-}6]$$

A theoretically distinct point (pH) exists for surfaces dominated by variable-charge colloids, where titration curves for different concentrations of non-specifically adsorbing electrolytes intersect. This demonstrates the lack of influence of electrolyte concentration on adsorption of H^+ or OH^- (i.e. PZSE) (Hendershot and Lavkulich, 1983; Uehara and Gillman, 1981) and applies to all charged surfaces of a soil suspension.

The PZNPC, like the PZSE, is measured via potentiometric titration, but in this case only surface functional groups on the soil solids that are proton-selective are titrated (Charlet and Sposito, 1987; Sposito, 1984). The PZSE = PZNPC only if all adsorbed protons result in changes in surface charge ($\sigma_O = 0$) and the net adsorbed ion charge at the PZNPC is independent of *I*. Several researchers have reported that PZSE does not necessarily correspond to a pH where $\sigma_H = 0$ (PZNPC) (Chorover and Sposito, 1995; McBride, 1994; Sposito, 1989). As an example, in complex soil systems composed of permanent and variable-charge surfaces, H^+ may exchange with counterions associated with permanent negative charge sites resulting in proton consumption with no net change in surface charge. Furthermore, at low pH, protons may be consumed in mineral dissolution reactions which again would not directly influence surface charge (σ_H).

Comparisons of PZSE and PZNPC values obtained by others shows some discrepancy. The PZNPC found for kaolinite ($\sigma_O \approx 0.8$ $mmol_c$ kg^{-1}; Brady et al., 1996) by several researchers (Motta and Miranda, 1989; Schindler et al., 1987; Xie and Walther, 1992; Zhou and Gunter, 1992) was between 4 and 5 compared to PZSE values around 3 found by Gallez et al. (1976) and Hendershot and Lavkulich (1983) for the same material. In spite of these differences, the PZSE is the most widely reported and

determined point of zero charge (Sparks, 1995), which gives credence to its consideration in this study.

The PZNC, as determined by ion adsorption assays, is the point (pH) where the sum of non-specifically adsorbed index cations (e.g. Na^+ or K^+) and anions (e.g. Cl^-, and NO_3^-) is equivalent (Eq. 3-4; Lewis-Russ, 1991). Lastly, the pH at which the electrical potential in the double layer at the plane of shear (zeta, ζ, potential) vanishes ($\sigma_P = 0$) is called the PZC. Since $\sigma_P = 0$, it follows from Eq. (3-2) that there is no net charge from the ions adsorbed in the diffuse swarm ($\sigma_D = 0$). The PZC is usually obtained by determination of the pH at which soil particles do not move in an applied electric field (electrophoretic mobility) (Sposito, 1989). The isoelectric point (IEP), as measured by electrophoretic techniques, can be defined as the pH where electrophoretic mobility is zero or electrokinetic charge measurements show a sign reversal for ζ (van Olphen, 1977). Thus, the PZC is synonymous with the IEP.

Theoretically and according only to the applicability of the balance of surface charge (Eq. 3-2), a system containing a charged surface (e.g. synthetic resin) that is immersed in a 1:1 electrolyte solution composed of non-specifically adsorbing ions, such as NaCl which forms only outer-sphere surface complexes, could exhibit a distinct pH where PZSE = PZNC = PZC. The requirements for such a system are stringent. The surface would have to be composed entirely of amphoteric sites ($\sigma_O = 0$) where H^+ and OH^- are potential determining ions while the net adsorbed ion charge was independent of *I*. Also, according to Eqs. (3-4 to 3-6), σ_{OS}, σ_{IS}, and σ_H would each have to be zero such that $\sigma_P = 0$ ($\sigma_D = 0$ from Eq. 3-2). In a natural soil setting, the above scenario is highly unlikely. Furthermore, the PZSE will only serendipitously be equivalent to the PZNC

and IEP as it is not a pH value where surface charge necessarily disappears. Its relationship to the other points of zero charge is indirect (Sposito, 1984; 1989).

In summary, the various points of zero charge will be referred to in the following fashion: the pH of intersection of titration curves of varying I will be called the PZSE; the pH where the net amount of non-specifically adsorbed cations and anions is the same is the PZNC; and the pH where ζ shows a sign reversal is the IEP.

Several articles have been published comparing potentiometric titration (PZSE) to ion adsorption techniques (PZNC) for the determination of the point of zero charge in soils and pure minerals. Generally, there is not a good correlation between the two measures (Gallez et al., 1976; Hendershot and Lavkulich, 1983; Marcano-Martinez and McBride, 1989; van Raij and Peech, 1972). This has been attributed to the presence of permanent negative-charge colloids in the soil system (Marcano-Martinez and McBride, 1989), the presence of strongly adsorbed Al^{3+} remaining on permanent negative-charge sites in the system via the potentiometric titration method as opposed to its displacement during ion adsorption measurements (van Raij and Peech, 1972), and differences in pH where a balance exists between the adsorption of H^+ and OH^- (potentiometric titration) and the anion and cation of an electrolyte (ion adsorption) (Hendershot and Lavkulich, 1983).

Lavardiere and Weaver (1977) found good agreement between PZSE and PZNC for several spodic horizons dominated by sesquioxides and organic matter. This condition may be fulfilled only when the amount of H^+ or OH^- adsorbed on exchange sites equals that of the index cation or anion, respectively, suggesting that hydration energies of competing ions are similar (Sposito, 1981). Yopps and Fuerstenau (1964)

found excellent agreement between the points of zero charge determined by potentiometric titration and microelectrophoresis when analyzing mineral-standard α-alumina (Al_2O_3).

Current literature does not include work comparing point of zero charge values found by chemical methods such as potentiometric titration (PZSE) and ion adsorption (PZNC) with electroacoustic determinations (IEP), which were done using an AcoustoSizer™ (AZR) in our study. The AZR relates particle sound wave generation, the electroacoustic effect, to the frequency-dependent electrophoretic mobility from which the ζ potential is calculated by the instrument's software. Advantages of this technique compared to other instruments using electrophoretic mobility for size and/or charge determinations (e.g. dynamic light-scattering spectroscopy and microelectrophoresis) include the ability to work with relatively high suspension concentrations (1 to 40 $\%_v$ compared to concentrations of $< 0.01\ \%_v$ with the other techniques), negating the need for dilution of slurries. Furthermore, whereas microelectrophoresis, potentiometric titration, and ion adsorption generally require the preparation of several, pH-adjusted samples to span a particular point of zero charge, the AZR equipped with auto-titrator and large sample cell (350 mL) allows point of zero charge determinations using a single sample. Therefore, a material's point of zero charge may be determined in a fraction of the time (1.5 h) required for its measurement via traditional methods. It usually takes several hours to days to determine points of zero charge via potentiometric titration, ion adsorption assay, and most microelectrophoresis techniques.

There are, however, some potential drawbacks to using the AZR for surface charge determination of soils. The instrument relies on the measurement of sound-wave generation by relatively small charged particles. A potential disadvantage for its use in point of zero charge determinations for soils is the narrow range of particle sizes (0.1 to 10 μm) where surface charge measurements may be obtained. Moreover, the instrument was not specifically developed to resolve the electrophoretic mobility of charged particles in whole soils. Therefore, its ability to accurately determine ζ potential in these complex systems has not been demonstrated.

Due to the above listed advantages as well as potential drawbacks to electroacoustic mobility determinations in complex soil and mineral systems, the instrument was used along with two common chemical methods to determine the points of zero charge of several amphoteric materials. The objectives of this research were i) to assess the pH-dependent surface charge of mineral-standard kaolinite, synthetic goethite, as well as surface horizons of an Oxisol and Ultisol from Puerto Rico and ii) to determine the various points of zero charge of these materials via potentiometric titration, ion adsorption, and electroacoustic mobility.

Materials and Methods

Materials

The surface horizons (0 - 15 cm) of two tropical soils were obtained from the island of Puerto Rico. An Oxisol (clayey, oxidic, isohyperthermic Typic Acrorthox) sampled near Mayaguez on the west coast and an Ultisol (clayey, mixed, isohyperthermic

Typic Tropohumult) taken from the central mountainous area near Corozal were used in this study.

Poorly crystallized kaolinite (KGa-2) (powder form) was purchased from the Source Clay Minerals Repository (Columbia, MO). X-ray diffraction (XRD) analysis using CuKα radiation and aluminum side powder mounts (Whitting and Allardice, 1986), coupled with thermal gravimetric analysis (TGA), confirmed that the samples contained kaolinite as the dominant mineral phase (> 93 % pure). Goethite was synthesized using the methods of Atkinson et al. (1967) and Coughlin and Stone (1995). Briefly, 6.5 L of 0.5 *M* $Fe(NO_3)_3$ dissolved in 0.21 *M* HNO_3, was slowly added to 12.6 L of 1.55 *M* KOH, in plastic, while sparging with air. The suspension was then aged for 36 h in an oven at 70°C. After the supernatant was siphoned off, the suspension was washed 10 times with NANOpure™ (Barnstead/Thermolyne Corp., Chicago, IL) water to wash out any entrained salts. Surface properties of goethite prepared in a similar manner are discussed elsewhere (Atkinson et al., 1967; Balistrieri and Murray, 1981; Balistrieri and Murray, 1982). Suspended material was deposited on ceramic tiles for XRD analysis (Whitting and Allardice, 1986). The X-ray diffractograms coupled with TGA data confirmed Fe(O)OH to be the only mineral phase present. The material was then freeze-dried overnight at -46°C to obtain a solid, and the solid material was passed through a 0.5 mm sieve. The BET-N_2 specific surface areas (Quantachrome Corporation, 1996) of kaolinite and goethite were 18.1 and 70.2 $m^2\ g^{-1}$, respectively.

General Analytical Methods

Pertinent properties of the soils used in this study are presented in Table 3-1. The pH readings were taken in water at 1:10 soil to water ratio in order to model the CEC and AEC values (same soil to water ratio) measured in the ion adsorption portion of the experiment. Effective CEC was extrapolated from ion adsorption curves at 0.001 *M* ionic strength (*I*) at field pH (1:10 soil:water ratio) as this *I* was most representative of soil *I*.

Table 3-1. Pertinent chemical and physical characteristics of samples.

	Organic C	pH†	ECEC	Mineralogy‡	Texture§	Surface area
Sample	%		$mmol_c\ kg^{-1}$		---- % ---	$m^2\ g^{-1}$
Oxisol	2.4	5.2	9.0	k>go>gi≈q	10-34-56	41.9
Ultisol	1.1	4.9	50.1	k>q>is>go>m	12-29-59	37.8

†1:10 soil to water ratio.
‡k = kaolinite, go = goethite, gi = gibbsite, is = interstratified smectite, q = quartz, m = mica.
§sand – silt – clay; based on Fe oxide removal.

Mineralogy of the soil clay fractions (< 0.2 μm) was determined via X-ray diffraction (XRD) analysis using CuKα radiation. Magnesium- and K-saturated samples were scanned at 2° 2θ/min on ceramic tiles at 25°C. The K-saturated tiles were further scanned following heat treatments of 110°C, 300°C, and 550°C (Whitting and Allardice, 1986). Thermal gravimetric analysis (25°C to 1000°C) was used to confirm and supplement the XRD data. Particle size was determined by the pipette method (Gee and Bauder, 1986) following removal of iron oxides by dithionite-citrate-bicarbonate (Mehra and Jackson, 1960). Organic C content was determined by $K_2Cr_2O_7$ digestion (Nelson

and Sommers, 1996). Specific surface areas were obtained via 6-point BET-N_2 adsorption (Quantachrome Corporation, 1996).

Determination of Electric Charge

All experiments for charge determination were carried out under ambient laboratory conditions (temperature = 25±3° C), as prior experiments showed that ingress of CO_2 into solutions containing synthetic goethite was not important in lowering pH.

Potentiometric titration

Prior to analysis, soils were washed with 0.001 *M* HCl by shaking for 2 h followed by centrifugation which lowered soil pH ≈ 1.5 units compared to a water wash at the same soil to water ratio. This was performed to saturate the materials with H^+ in an effort to drive any reactions involving consumption of H^+ (i.e. amorphous mineral dissolution) not resulting in surface charge. Mineral dissolution was tested via analysis of Al, Fe, and Si in the supernatant compared to amounts of these elements extracted by washing with 0.0005 *M* $CaCl_2$. Analysis of the elements was performed by inductively coupled argon plasma-atomic emission spectroscopy (ICAP-AES) and indicated that mineral dissolution was insignificant resulting in < 0.1 % of total Al, Fe, or Si being dissolved. In order to ensure low amounts of salt were entrained, washing was repeated with NANOpure™ water until no precipitate (AgCl) was formed in the supernatant upon addition of 2 *M* $AgNO_3$, when the electrical conductivity (EC) was < 0.01 dS m^{-1}.

The potentiometric titration method of Marcano-Martinez and McBride (1989) and van Raij and Peech (1972) was used for all materials. To 50 mL beakers were added 4 g air-dried material and 10 mL of electrolyte solution (0.1, 0.01, and 0.001 *M* NaCl).

Increasing amounts of standardized 0.1 *M* HCl or 0.1 *M* NaOH were then added in order for the pH of the samples (for each electrolyte concentration) to range from ≈ 2 to 9. The beakers were then filled to 25 mL with NANOpure™ water.

Samples were then covered and mixed several times by manual agitation over an incubation period of 7 d. Bioactivity in the supernatant solutions was not apparent throughout the course of the experiment. Soil pH was measured at the end of the incubation period. Amounts of H^+ and OH^- adsorbed by a material were determined by subtracting the amount of HCl or NaOH required to bring 10 mL of electrolyte plus 15 mL of water (no soil) to the same pH.

Ion adsorption

Determination of CEC and AEC for charged surfaces (dominated by variable-charge colloids) as a function of pH and *I* can be accomplished via the ion adsorption method. The point (pH) where non-specific surface adsorption of anions and cations is equivalent is defined as the PZNC. Positive and negative charges were estimated by the measurement of Na^+ and Cl^- retention in soils and pure minerals as a function of pH and *I*. A modified method of Marcano-Martinez and McBride (1989) and Schofield (1949) was used. Air-dried samples of 2 g (< 0.5 mm) were placed in preweighed 30 mL polyethylene centrifuge tubes to which 20 mL of 1 *M* NaCl was added. The samples were shaken for 1 h and centrifuged, with the supernatant being discarded. Amounts of 20 mL of 0.5 *M* NaCl were then added to the tubes, with sample pH being adjusted with HCl or NaOH to span the expected points of zero net charge. This was followed by 12 h of shaking, centrifugation, and supernatant removal. The 0.5 *M* NaCl wash and pH adjustments were performed 2 more times, with shaking times of 1 h. The rigorous

washing procedure was carried out to ensure exchange sites were saturated with Na^+ and Cl^-. Five washes were then performed with 20 mL of 0.01 and 0.001 *M* NaCl, with pH readjustment and shaking for 1 h between washes. This was done to determine the effect of varying *I* on retention of ions. Ionic strengths of typical non-saline temperate-region soils are < 0.05 *M* (McBride, 1994), whereas their tropical counterparts are < 0.005 *M* (Gillman and Bell, 1978). The *I* values of the two soils used in this study were estimated at 0.003 *M* each, following the method of Gillman and Bell (1978).

After the final NaCl wash, supernatant pH (equilibrium pH) was measured. The supernatants were discarded and samples weighed to compensate for any entrained NaCl solution. Adsorbed Na^+ and Cl^- were then displaced by 5 washings with 20 mL aliquots of 0.5 *M* NH_4NO_3. Extracts were combined and filtered through 0.45 µm Millipore™ nylon filters and stored in a refrigerator, at 4° C, prior to analysis. Concentrations of Na^+ (determined by ICAP-AES) and Cl^- (found colorimetrically; Domask and Kobe, 1952) displaced were corrected for occluded NaCl in the soil volume and used as measures of negative and positive charges, respectively.

Electrophoretic mobility

The isoelectic point (IEP) was ascertained with the AZR (Colloidal Dynamics, Warwick, RI) which relies on measurement of electroacoustic parameters for determination of particle charge and size. Assessment of electroacoustic principles specifically related to the operation of the AZR have been described in detail elsewhere (Colloidal Dynamics, 1996; O'Brien et al., 1995; O'Brien and Rowlands, 1993; Rowlands et al., 1997). Briefly, application of an alternating electrical field to a colloidal suspension results in the generation of acoustic waves created by the compression and

rarefaction of the suspension. This phenomena is known as the Electrokinetic Sonic Amplitude (ESA) effect from which the AZR is able to determine particle size and charge. The instrument applies the variable voltage to parallel plate electrodes that contact the colloidal suspension. The electrical field created by the alternating voltage causes the particles to move at certain velocities depending upon their size, charge (ζ potential), and the frequency of the applied field assuming a density difference between the particles and the supporting fluid matrix. Particle movement results in sound wave generation (ESA effect) and measurement of this effect yields information about the particles' motion. These measurements enable the determination of suspended particle velocity over a range of 8 excitation frequencies (0.3 to 11.5 MHz) which, grouped together, is called the dynamic mobility spectrum of the particle. Particle charge and size can be extracted from the dynamic mobility spectrum of the particle. This information is then related to the particle's frequency-dependent electrophoretic mobility from which the instrument's software calculates the ζ potential (O'Brien et al., 1995).

At the highest frequency of the dynamic mobility spectrum (11.5 MHz), inertia becomes an important factor for particles < 0.1 μm in diameter making this the lower limit for size detection. However, the AZR is capable of reliably measuring the ζ potential for particles at and slightly below this size. At the other extreme, the mobility of particles with diameters > 10 μm is too small to accurately measure. This explains why this value represents the upper limit for size and charge determinations (O'Brien et al., 1995). Thus, ζ potentials of suspended sand and silt sized particles were not measured.

It is important to point out here that the reactive size fraction of soils (e.g. clay fraction at < 2 μm) fall within the ζ potential detection limits of the instrument. Furthermore, the AZR allows resolution of the charge and size of spheres and spheroids (discs and rods) which is necessary for accurate descriptions of soils and soil minerals. This is because the dynamic mobility spectrum for a spheroidal particle has a very similar shape to that of a sphere (Colloidal Dynamics, 1996; O'Brien et al., 1995). Comparison of ζ potential data for minerals obtained by microelectrophoresis and the AZR agrees reasonably well indicating the accuracy of the AcoustoSizer™ (Table 3-2).

Table 3-2: Comparison of AcoustoSizer™ ζ potentials (mV) with those using standard microelectrophoretic measurements.

Colloid	pH	AcoustoSizer™	Microelectrophoresis†
TiO_2	4.0	37	38
	4.0‡	40	50, (57)
	8.2	-6	-6
	9.0	-20	-22
Si_3N_4	3.5	26	24
	8.9	-39	-43
	10.0‡	-35	-42, (-51)
Kaolin	4.4	-28	-26
	9.8	-37	-43
Alumina	5.0	47	58, (53)

Adapted from Colloidal Dynamics, 1996.
†Measured with Rank Bros. Mark II and Malvern ZetaSizer (in parentheses).
‡Material from a different source.

Soils were prepared following the same protocols as described for potentiometric titration. Prior to ζ potential measurements by the AZR, equipped with double-junction pH glass electrode and auto-titrator, samples were mixed mechanically in 0.01 and 0.001 *M* NaCl and made up to concentrations of 5 $\%_v$ (except for synthetic goethite which was

made up to 0.5 %$_{v}$). The titrants were 1 *M* HCl and 1 *M* NaOH and samples were titrated ≈ ± 1 pH units from their points of zero charge as determined by potentiometric titration and ion adsorption, with a back-titration being performed on all samples. The back-titration was carried out in order to determine if the material surfaces changed, as measured by changes in ζ potential, from titrating on both the acid and alkaline side of the IEP.

Statistical Methods

One-way analysis of variance was used to statistically compare differences between methods and electrolyte concentrations. Statistically significant differences between electrolyte concentrations were only evaluated for the points of zero charge found by ion adsorption and electrophoretic mobility.

Results and Discussion

Potentiometric Titration

The PZSE is the pH where the net adsorption of potential-determining ions, H^+ and OH^-, on variable-charge surfaces is independent of electrolyte concentration. Titration curves at varying *I* will show a common intersection point (PZSE) when pH is plotted vs. surface charge or amounts of acid or base added. In our experiment, the two soils clearly demonstrated points where salt concentration had no effect on adsorption of potential-determining ions over the pH ranges measured (Fig. 3-1). However, the PZSE of mineral-standard kaolinite and synthetic goethite demonstrated a slightly different trend than the soils. The titration curves of the mineral samples did not follow the usual

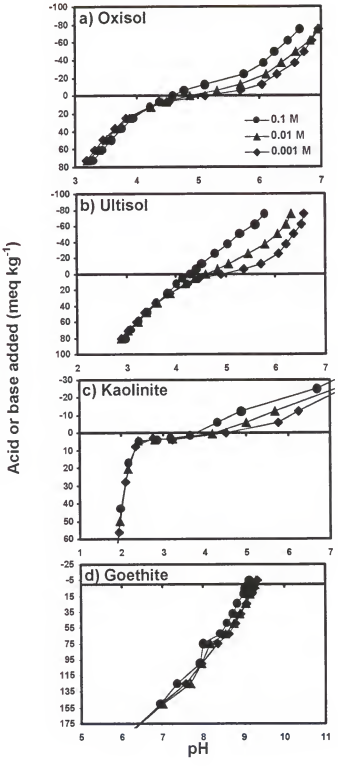

Figure 3-1: Potentiometric titration curves of an Oxisol (a), Ultisol (b), kaolinite (c), and goethite (d) as a function of pH at different ionic strengths.

trend of higher electrolyte concentration resulting in higher pH below the PZSE. It is possible, at lower pH values, that protons were predominantly consumed in mineral dissolution reactions instead of generating surface charge (Lindsay, 1979). This would have the effect of narrowing the margin of difference between various electrolyte titration curves, which was evident. It is postulated that the effect described above was not as important for the two soils, which had varied mineralogy (Table 3-1). Moreover, all the samples demonstrated increased separation between titration curves at pH values above the PZSE. Above this point material buffering capacity is reduced, which is manifested via relatively small increases in pH resulting in large expansion in charge generation.

Figure 3-1 clearly displays, for both soils and the pure minerals, that PZSE was on the acid side or below the point where equal amounts of acid and base were added (acid side of the zero point of titration). This may be explained by the fact that the current method did not account for the surface charge on the solids at the onset of the potentiometric titration. The adsorbed H^+ and OH^- were measured relative to a blank solution and not to a common value of surface charge on the solids. This was especially evident for synthetic goethite. This material had relatively high surface area (70.2 $m^2\ g^{-1}$) and was prepared in strong base (1.55 *M* KOH). Thus, its surface was highly buffered and able to adsorb protons well below the point of equal addition of acid and base before showing a crossover of *I* curves at pH 7.9.

Despite greater percentage of organic carbon in the Oxisol soil (2.4 %) as compared to the Ultisol soil (1.1 %), which tends to lower the point of zero charge (van Raij and Peech, 1972), the PZSE of the Oxisol (4.2) was higher than that of the Ultisol (3.7). Fox (1982) found similar values (4.4 and 3.2, respectively) for these soil series

when employing a comparable methodology. Though the mineralogy of the two soils consisted of relatively large quantities of high point of zero charge sesquioxides (~ 44 % and 17 %, respectively), the presence of organic matter, kaolinite, and SiO_2 in these samples tends to reduce the point of zero charge. Furthermore, larger quantities of Fe and Al oxides (PZSE > 6.5) in the Oxisol (< 2 μm fraction) gave this soil a higher PZSE whereas the Ultisol possessed greater amounts of low point of zero charge minerals (PZSEs for $SiO_2 \approx 2$ and kaolinite $\approx 2.5 - 3.5$) as well as some permanent surface-charge minerals, which gives rise to a slightly lower PZSE (Atkinson et al., 1967; Gallez et al., 1976; Parks and de Bruyn, 1961).

Kaolinite had a PZSE of 2.8 in this study, which is consistent with work done by Gallez et al. (1976) and Hendershot and Lavkulich (1983) (PZSEs = 2.8 and < 3, respectively). Literature-reported PZSE values of synthetic goethite are between 7 and 9 (Atkinson et al., 1967; Schwertmann and Taylor, 1989). The result found in this experiment (7.9) was in the middle of this range.

Ion Adsorption

The amounts of adsorbed Na^+ and Cl^- of the four materials used in this study varied as a function of both pH and *I* (Fig. 3-2). The pH where cation adsorption was equal to anion adsorption was obtained by interpolating between the AEC and CEC curves. All materials exhibited a decrease in the PZNC, or increase in negative surface charge, with increasing *I*. This is consistent with the theory of the electric double layer (EDL) for variable-charge colloids which states that increasing solution *I* yields an increase in the magnitude of the surface charge. Our samples were net negatively

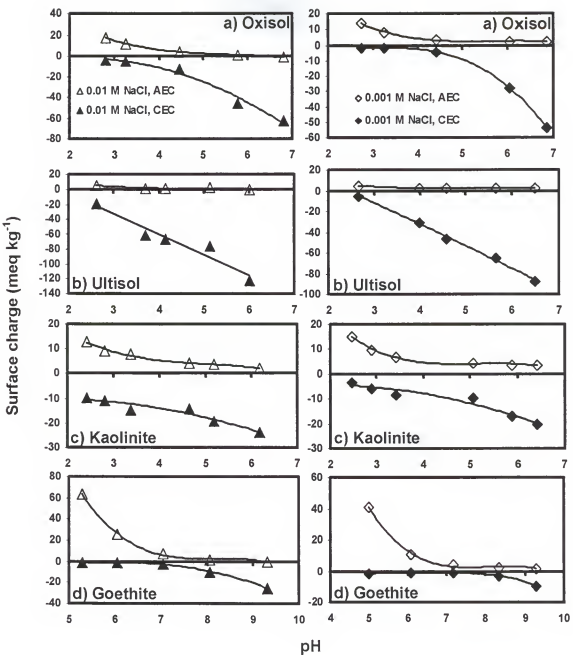

Figure 3-2. AEC and CEC of an Oxisol (a), Ultisol (b), kaolinite (c), and goethite (d) as a function of pH and ionic strength.

charged at equilibrium solution pH (Table 3-1), thus, increases in solution *I* should and did decrease their PZNC values. Furthermore, this phenomena has been described by other researchers (Chorover and Sposito, 1995; van Raij and Peech, 1972).

Based on the Gouy-Stern theory of the EDL (van Olphen, 1977), for a constant surface-potential material, the magnitude of its surface charge is proportional to the square root of the electrolyte concentration. Therefore, under equilibrium conditions for a material with a net negatively-charged surface (pH > PZNC), increasing solution *I* will result in increased negative surface charge and lowered PZNC as surface protons are exchanged for electrolyte cations (Uehara and Gillman, 1981). This was demonstrated by Gallez et al. (1976), Morais et al. (1976), and van Raij and Peech (1972) for highly weathered tropical soils from Nigeria and Brazil. Furthermore, soil pH determined at a 1:10 soil:water ratio (Table 3-1) compared to a 1:10 soil to either 0.01 or 0.001 *M* NaCl ratio showed the pH values in water to be above those determined in salt solution (Fig. 3-2). Therefore, under natural condition, both soils in our study had net negatively-charged surfaces (pH > PZNC).

Above pH 4.5, for 0.01 and 0.001 *M* NaCl solutions, the Oxisol possessed $\leq$ 12.5 and 4.2 $mmol_c\ kg^{-1}$ of positive charge, respectively (Fig. 3-2a). At pH $\approx$ 6.5, only the 0.001 *M* NaCl curve showed 2.4 $mmol_c\ kg^{-1}$ of positive charge, possibly indicating the existence of some protonated surfaces not neutralized by anion adsorption (Marcano-Martinez and McBride, 1989; van Olphen, 1977). At low pH ($\approx$ 2.5), $\approx$ 4.4 and 1.5 $mmol_c\ kg^{-1}$ of negative surface charge remained for the 0.01 and 0.001 *M* NaCl curves, respectively. This was most likely due to strongly acidic, dissociated, organic functional groups (van Raij and Peech, 1972). Cation exchange capacity generally increased from the low at pH 2.5 and displayed highs of 62.6 (0.01 *M*) and 53.3 $mmol_c\ kg^{-1}$ (0.001 *M*), respectively, just above pH 6.5. The PZNCs for this soil in solutions of 0.01 and 0.001 *M* NaCl were 3.7 and 4.3, respectively (Table 3-3).

For the pH ranges measured, the Ultisol showed very little AEC for both the 0.01 and 0.001 *M* NaCl curves (Fig. 3-2b). The highest values around pH 2.6 were 5.2 and 4.7 $mmol_c\ kg^{-1}$ of positive charge, respectively. Even at this low pH, however, CEC was higher for both electrolyte concentrations which is common for soils possessing 2:1 phyllosilicates (Table 3-1; Hendershot and Lavkulich, 1983). The PZNCs determined were very low at 2.3 and 2.6 for the 0.01 and 0.001 *M* NaCl solutions (Table 3-3), respectively. The difference in CEC and AEC of the Ultisol as compared to the Oxisol appeared largely due to mineralogy. The presence of colloids possessing permanent negative charges (~ 25 % interlayered smectite) as well as an abundance of low point of zero charge minerals (~ 25 % SiO_2; PZNC 2.0 to 3.0) in the former soil resulted in the PZNC being nearly unobserved over the pH ranges measured, especially at 0.01 *M* NaCl (Table 3-3).

In the pH range measured (2.4 to 6.4) (for a given salt concentration), mineral-standard kaolinite had similar values of AEC and CEC (Fig. 3-2c). At the most acidic pH values measured, AECs were 12.9 and 15.3 $mmol_c\ kg^{-1}$ (0.01 and 0.001 *M* NaCl, respectively). Cation exchange capacities, at the highest OH^- concentrations, had ≈ 24.0 and 20.3 $mmol_c\ kg^{-1}$ (0.01 and 0.001 *M* NaCl, respectively) of negative surface charge. The PZNC of 3.5 (0.001 *M* NaCl) was close to the range of 4.0 to 5.0 for this material as reported by Ferris and Jepson (1975), Sposito (1989), and Zhou and Gunter (1992).

As a result of synthetic goethite's high specific surface area (70.2 $m^2\ g^{-1}$) and the pH range measured (5.0 to 9.5), the material had an abundance of positive surface charge at both electrolyte concentrations (Fig. 3-2d). Though having AECs of 63.4 and 41.0 $mmol_c\ kg^{-1}$ at pH near 5, this parameter was almost non-existent when pH was raised to ≈

9.3 at both *I* values. Cation exchange capacity did not reach values above 10 $mmol_c\ kg^{-1}$ until pH was raised above 8 at both salt concentrations. This phenomenon is typical for goethite, as Sposito (1989) has reported the material's PZNC to be between 7.0 and 8.0. These values are in close agreement to the numbers determined in this experiment (7.3 and 8.4). Furthermore, the magnitude of charge on goethite surfaces, at pH ≈ 5, was high due largely to its high specific surface area (70.2 $m^2\ g^{-1}$).

Electrophoretic Mobility

According to Eq. (3-5), the PZC (or IEP) of a variable-charged particle in solution is defined as the pH where the net total particle charge is zero ($\sigma_P = 0$). This parameter is commonly determined from electrophoretic mobility (van Olphen, 1977); however, such a measurement for soils, using an acoustic detector, has not yet been reported in the literature.

The heterogeneous nature of surface charge in soils results in the formation of an IEP continuum. For example, at pH 5, a soil possessing only kaolinite and goethite would have negatively charged kaolinite surfaces and positively charged goethite surfaces. Kaolinite particles would move toward a positively charged pole while the opposite would be true for goethite. Thus, the IEP of a soil, as measured by the AZR, would be an average of the mobilities of the charged particles (≈ 0.1 to 10 μm particle size) in the system.

Figure 3-3 presents ζ potentials of the soils and mineral-standards as obtained by the AZR. Individual IEPs were found by first titrating with acid to pH < IEP followed by addition of base back to a pH value near the starting point. It was expected that the IEP

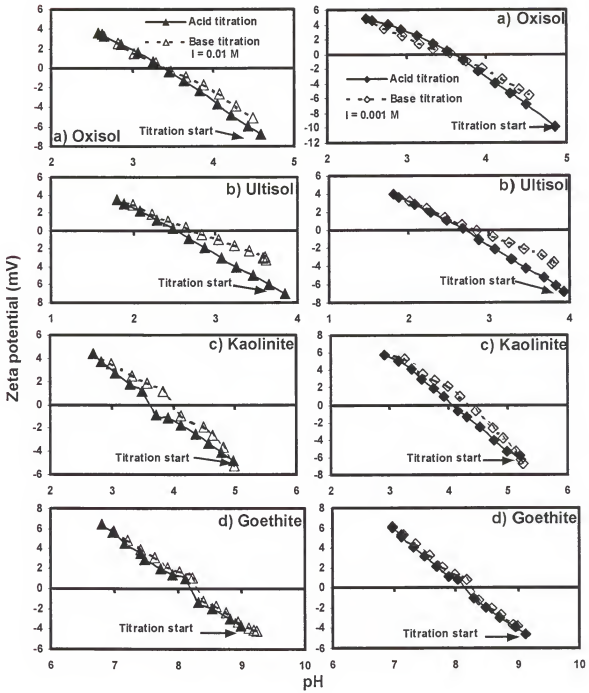

Figure 3-3. IEP, as found by the AZR, of an Oxisol (a), Ultisol (b), kaolinite (c), and goethite (d) as a function of pH and ionic strength.

of the first pass (i.e. 1st titration from alkaline to acid side of the IEP) would be higher than the IEP of the second pass (i.e. 2nd titration from acid side to alkaline side of IEP). This was because additions of acid or base were increasing solution *I* and should have compacted the EDL which subsequently should have decreased ζ and, thus, the measured IEP. In all cases, however (except for the Oxisol curve at 0.001 *M* NaCl), the IEP was greater when back-titrating with base, which appears to be a systematic effect.

The differences in IEP when performing the back-titration were generally small, and in all cases, IEPs were obtained via interpolation between the two curves. It is reasonable to conclude the generally slight differences in the curves may have arisen from mineral dissolution and reprecipitation reactions that occurred during the titrations. This changes the surface-charge properties of the materials. Furthermore, in the case of synthetic goethite, the titration curves suggest few or no problems related to the ingress of CO_2 and subsequent formation of HCO_3^- which was most likely due to its high surface area. This was because the IEP changed little over the course of the experiment ($\sim + 0.2$ pH units). In an experiment determining ζ potentials for gibbsite between pH 7 to 12 (in air), Rowlands et al. (1997) did not observe problems associated with formation of HCO_3^-.

The materials displayed only slight differences in IEPs between the two background electrolyte solutions (Table 3-3). The IEPs were generally a tenth to a few tenths of a pH unit lower in the 0.01 *M* solutions as compared to the 0.001 *M* ones. These findings are consistent with the theory of the EDL. Theory states that increasing electrolyte concentration results in a decrease in the thickness of the double layer, lowering colloid mobility, ζ potential, and charge at the plane of shear while shifting the

IEP to lower values (Zhang and Zhao, 1997). Research performed by O'Brien et al. (1995) at low electrolyte concentrations (< 0.01 *M*), using the AZR, confirm this trend. They have shown that increases in electrolyte concentration resulted in decreases in the electrophoretic mobility as well as the absolute value of charge at the plane of shear for titanium oxide and gibbsite. However, in our experiment, this trend was reversed with synthetic goethite, though the difference was small (0.1 pH unit).

It is interesting to note that the pH vs. ζ potential curves for soils had nearly linear slopes over the pH ranges studied while the mineral-standards, especially the kaolinite in 0.01 *M* NaCl and synthetic goethite at both *I* values, showed evidence for a discontinuity in the curves near the IEPs (Fig. 3-3). The sensitivity of the instrument decreases with decreasing particle charge (Colloidal Dynamics, 1996), possibly giving rise to the discontinuities evidenced in the mineral-standard curves. A possible explanation for the lack of this effect in the soils is that the heterogeneous nature of the charged surfaces in these materials could have led to enhanced buffering of surface charges and stronger signals near and around the IEP. As the mineral-standards were nearly pure, this effect would not be manifested for such samples.

Table 3-3. Summary of the points of zero charge of two soils, kaolinite, and goethite as measured by potentiometric titration (PZSE), ion adsorption (PZNC), and electroacoustic mobility (IEP).

	PZSE	PZNC		IEP	
		NaCl (moles L^{-1})			
Sample		0.01	0.001	0.01	0.001
Oxisol	4.2	3.7	4.3	3.4	3.5
Ultisol	3.7	2.3	2.6	2.6	2.7
Kaolinite	2.8	2.7	3.5	3.8	4.1
Goethite	7.9	7.3	8.4	8.2	8.1

Currently, there is little information available on electroacoustic detection of particle mobility for determination of amphoteric particle IEPs. However, the same mineral-standard kaolinite as used in this research was found to have IEPs ranging from 3 to 5 (avg. ≈ 4.0±0.9) as found by electrophoretic mobility techniques by several researchers (Braggs et al., 1994; Carroll-Webb and Walther, 1988; Ferris and Jepson, 1975; Parks, 1967). Our values of 3.8 and 4.1 (0.01 and 0.001 *M* NaCl, respectively) found by the AZR were within the range and near the average of those values found above. Furthermore, according to Bleam and McBride (1984), Djafer et al. (1991), Matis et al. (1999), Su and Suarez (1997), Weesner and Bleam (1998), and Zhang (1997) synthetic goethite, prepared in a similar fashion as for the present study, has IEP values as measured by electrophoretic mobility ranging from 7.5 to 9.3 with the average of their reported values being ≈ 8.6±0.6. This can be compared to our values of 8.2 and 8.1 (0.01 and 0.001 *M* NaCl, respectively) as determined by the AZR (Table 3-3). Therefore, the IEPs found by the AZR for goethite were, much like kaolinite, within the range of previously reported data for this material.

Comparison of the Three Points of Zero Charge

One-way analysis of variance showed that differences between methods (PZSE vs. PZNC in 0.001 *M* NaCl vs. IEP in 0.001 *M* NaCl; PZSE vs. PZNC in 0.01 *M* NaCl vs. IEP in 0.01 *M* NaCl) and electrolyte concentrations (PZNC in 0.01 vs. 0.001 *M* NaCl; IEP in 0.01 vs. 0.001 *M* NaCl; and PZNC vs. IEP in 0.01 and 0.001 *M* NaCl) were, in all cases, not significant ($p > 0.05$). Furthermore, ANOVA analyses between the PZSE, PZNC, and IEP values in 0.001 *M* NaCl gave a slightly higher p value (1.00) than the

similar comparison where PZNC and IEP were determined in 0.01 *M* NaCl ($p = 0.92$), suggesting more similarity between the former as compared to the latter. This is worth mentioning, for the *I* in tropical soils is generally low (e.g., < 0.005 *M*) and the *I* values for the soils used in this study were estimated to be ≈ 0.003 *M* each. In spite of the statistical similarities between methods, the assumption that PZSE = PZNC = IEP was not true in our experiment for the soils and kaolinite as these materials possessed permanent charge ($\sigma_0 \neq 0$) (see Eqs. 1-6). Furthermore, from Table 3-3, a practical difference was observed between the points of zero charge. Considering only points of zero charge at $I = 0.001$ *M* plus the PZSE data, though not significantly different, the range spanned from 0.5 (goethite) to 1.1 (Ultisol) pH units.

Conclusions

The three definitions of points of zero charge used in this experiment – PZSE, PZNC, and IEP - measure theoretically unique types of charge as evidenced by Eqs. (3-4 to 3-6) (Barrow, 1987; Sposito, 1989). Though analysis of variance yielded no significant differences between the points of zero charge, there were practical differences between the results generated by potentiometric titration (PZSE), ion adsorption (PZNC), and electroacoustic detection of particle mobility (IEP).

The question remains as to whether or not the points of zero charge determined accurately describe the parameter(s) they were measuring (Eqs. 3-4 to 3-6). Making comparisons of points of zero charge of mineral-standard kaolinite and synthetic goethite with literature values, as determined by other researchers, yielded points of zero charge that fell within the ranges of those reported. This is especially noteworthy for the AZR as

the potential drawbacks (see Introduction) to its use in complex systems were not necessarily realized when determining particle mobility via electroacoustic detection in our study.

It is reasonable to conclude points of zero charge determined by the AZR for kaolinite and goethite, in our experiment, adequately modeled this parameter. The ability of the instrument to quickly (1.5 h) resolve mobility of small (0.1 to 10 μm - which is within the active/clay fraction of soils) charged spheres, discs, and rods demonstrate its use for the determination of ζ potential and IEP in soils. Though more work must be performed using this instrument to enable generalizations regarding the AZR's performance in point of zero charge determinations for soil systems, the results are encouraging inasmuch as the time required to generate this value was drastically reduced compared to the potentiometric titration and ion adsorption methods.

The information gained in this study will be of great use for later studies focusing on Cd and Pb sorption. Surface charge characterization of the Oxisol and Ultisol soils as it varied with pH will enable a deeper understanding of how Cd and Pb are sorbed in highly weathered tropical soils. Also, knowing the pH values corresponding to the various points of zero charge will enable the elucidation of probable mechanisms of Cd and Pb sorption.

CHAPTER 4
CONCENTRATION, pH, AND SURFACE CHARGE EFFECTS ON Cd AND Pb SORPTION IN THREE TROPICAL SOILS

Introduction

Due to their low negative surface charge densities at common pH values (4 - 5), highly weathered tropical soils may exhibit relatively low affinities for heavy metals (McBride, 1994). The persistence and mobility of Cd and Pb in these soils are dictated by the extent to which the metals sorb to solid phases, which is a function of reactions affecting surface charge (i.e. pH and ionic strength; Naidu et al., 1997).

Increasing ionic strength (I) and the pH, above the point of zero charge in tropical soil systems increases negative surface charge (Marcano-Martinez and McBride, 1989; van Olphen, 1977; van Raij and Peech, 1972). Many researchers have shown increased Cd and/or Pb sorption in tropical soils and/or in pure oxidic mineral systems (i.e. goethite) with increasing pH (Bruemmer et al., 1988; Davis and Leckie, 1978; Kinneburgh et al., 1976; Naidu et al., 1994; Puls et al., 1991; Rose and Bianchi-Mosquera, 1993; Tiller et al., 1984a) due mainly to increased negative surface charge.

Little research has been done directly comparing surface charge with heavy metal sorption in variable-charge systems. Naidu et al. (1994) looked at the effects of this parameter on the sorption of Cd in some highly weathered soils while Haas and Horowitz (1986) did a similar experiment on kaolinite. Knowledge of surface charge as it changed with pH enabled these researchers to determine the point of zero charge. This

information allowed them to propose probable mechanisms of Cd sorption (i.e. molecular level information) from their macroscopic data.

Understanding mechanisms of metal sorption in soils is important as these reactions dictate the strength of the metal-soil surface interaction. The stronger the interaction of Cd or Pb with the soil surface, the less the likelihood of environmental contamination to plants and groundwater systems. On a relative basis, exchange reactions, which are classified as reversible electrostatic or outer-sphere reactions, render the metals most labile. Inner-sphere complex formation and co-precipitation with soil surfaces, which involve bond formation between contaminant metals and soil surfaces, cause the Cd and Pb to be retained strongly and in many cases nearly irreversibly (McBride, 1994).

The literature is replete with research considering the sorption of heavy metals in temperate region soils as a function of pH, *I*, initial metal concentration, and effect of background electrolyte. Relatively little has been published on the effects of these variables on Cd or Pb sorption in highly weathered tropical soils. The objectives of this research were to investigate how varying initial metal concentrations and soil solution pH and *I* affect surface charge as well as the sorption of Cd and Pb in tropical soils (Oxisol, Ultisol, and Mollisol).

Materials and Methods

Soil Samples

The surface horizons (0 - 15 cm) of three tropical soils from Puerto Rico were sampled between 1996 and 1998, air-dried, and ground to a particle size of 0.5 mm prior

to being used in this study. A Mollisol (fine loamy, mixed, isohyperthermic Cumulic Haplustoll) obtained from the Lajas Valley area near the southwest coast as well as the Oxisol (clayey, oxidic, isohyperthermic Typic Acrorthox) and Ultisol (clayey, mixed, isohyperthermic Typic Tropohumult) used in the previous chapter were used in this study. The soils were selected based upon their varying physicochemical properties. The important mineralogical and chemical properties of these soils were obtained using standard procedures (Chapter 3; General Analytical Methods section, pg. 28) and are presented in Table 4-1.

Table 4-1: Pertinent soil physicochemical properties.

	Organic matter	PZNC	pH	CEC	Sum H+Al	Total Fe+Al	Clay mineralogy[†]	Texture[‡]	Specific surface area
Sample	%			-- $cmol_c/kg$ --			%		$m^2\ g^{-1}$
Oxisol	4.1	3.7	4.9	3.1	1.7	28.7	k>go>gi≈q	10-34-56	41.9
Ultisol	1.9	2.3	4.7	11.0	7.1	8.6	k>q>is>go>m	12-29-59	37.8
Mollisol	1.2[§]	-	6.9	20.9	-	6.9	k>is/v>m>q	39-39-22	17.3

[†]k = kaolinite, gi = gibbsite, go = goethite, is = interstratified smectite, is/v = interstratified smectite + interstratified vermiculite, m = mica, q = quartz
[‡]sand – silt – clay
[§]Does not meet classification requirements for quantity of organic matter necessary for a Mollic epipedon (Soil Conservation Service, 1994), however, soil classified as Mollisol based on location from which sample was taken.

Soil pH measurements were made in H_2O (soil:solution ratio 1:2) using a pH meter equipped with combination gel-filled glass electrode. Specific surface areas were obtained via 6-point BET-N_2 adsorption (Quantachrome Corporation, 1996). The cation exchange capacity (CEC) was determined by adding the 1 *M* KCl extractable acidity to cations (Ca^{2+}, Mg^{2+}, Na^+, K^+) exchanged by neutral 1 *M* $NH_4C_2H_3O_2$ (pH 7) as described

in Thomas (1982). Total Fe and Al was determined by microwave digestion of soil samples according to U.S. EPA method 3051 (U.S. EPA, 1995). All metals were determined by either ICP-AES or flame AAS and analyses were performed on duplicate samples.

Determination of Cd and Pb Sorption

All experiments were performed under ambient laboratory conditions with no environmental gas control. Samples were not filtered before metal analysis on the flame AAS as prior experiments demonstrated no significant differences in metal concentrations between unfiltered samples and samples filtered through 0.45 μm Millipore filters. Furthermore, there were three replicates for each treatment.

Sorption isotherms as a function of initial Cd and Pb concentration

Sorption isotherms for Cd and Pb were determined in three soils to ascertain the effects of soil and metal on soil-metal sorption capacity. A method similar to that of Naidu et al. (1994) was used to construct Cd and Pb sorption isotherms. Soil (≈ 1 g) was equilibrated with 30 mL of aqueous solution for 24 h at 25±3°C on a reciprocating shaker in 50 mL polyethylene centrifuge tubes. Preliminary kinetic studies indicated that a 24 h reaction period was sufficient to achieve equilibrium conditions when using a reciprocating shaker. Aqueous solutions were prepared in $NaNO_3$ to have a final I of 0.01 M after addition of $Cd(NO_3)_2$ or $Pb(NO_3)_2$. The above ionic strength was chosen as preliminary experiments showed no significant differences between Cd and Pb sorption in solutions having I of 0.005 and 0.01 M. The former I value is representative of tropical soils (Gillman and Bell, 1978), whereas the later is typical of non-saline temperate soils

(McBride, 1994). Cadmium and Pb concentrations ranged from 0 to 1.2 m*M* as prior analysis demonstrated this concentration range allowed expression of the maximum metal sorption capacity of the Oxisol and Ultisol soils. After equilibration, the samples were centrifuged and the supernatant refrigerated (4° C) for later analysis of Cd and Pb on a flame AAS. The amount of Cd or Pb sorbed was calculated from the difference between the amount that was added and the portion remaining in solution after equilibration (soil blanks to which only 0.01 *M* $NaNO_3$ was added did not have a significant amount of either Cd or Pb).

Sorption of Cd and Pb as a function of pH

Sorption of Cd and Pb was determined at varying pH values to elucidate pH effects on surface charge and metal sorption in representative tropical soils. Soil solutions containing ≈ 1 g soil and 29 mL of 0.007 *M* $NaNO_3$ were prepared in 50 mL polyethylene centrifuge tubes. Suspension pH values of ~2 to 7 were attained by adjustment with either HNO_3 or NaOH. The solutions were shaken for 24 h at 25±3°C, after which the pH was measured and readjusted if necessary. This was performed until the suspension pH values were stable at the desired levels. One mL of Cd or Pb, as nitrate salts, was then added at a metal concentration of 36 m*M* so the final metal concentration and *I* in the suspensions were 1.2 m*M* and 0.01 *M*, respectively. After metal addition, the solutions were shaken for 24 h at 25±3°C. Suspension pH was measured and the samples were centrifuged. The supernatant was collected and analyzed for Cd, Pb, Al, and Fe on the flame AAS. Aluminum and Fe were measured to check for the dissolution of oxide minerals. It was found that at the lowest pH values (~ 2.5), < 2 % of the total Al and < 0.1 % of the total Fe was dissolved from the soil samples

indicating little oxide dissolution. Adjustment of pH affected I by a maximum of 20 % and sample volume by no more than 3 %.

Blank solutions containing only 1.2 mM $Cd(NO_3)_2$ or $Pb(NO_3)_2$ in 0.01 M $NaNO_3$ were titrated with NaOH to check for formation of solid phases. The addition of base yielded no precipitate in the presence of Cd in the pH range of this study. However, at pH $\geq$ 5.9 a solid phase was detected in the Pb-containing solution (supersaturated with $Pb(OH)_2$; Gustafsson, 2000).

Surface charge

To elucidate possible Cd and Pb sorption mechanisms in the Oxisol and Ultisol, negative surface charge was estimated by measuring Na^+ retention as a function of pH (in the absence of Cd^{2+} or Pb^{2+}; I = 0.01 M) and compared to the amount (equivalents; $mmol_c$ kg^{-1}) of sorbed Cd and Pb. The negative surface charge of kaolinite (Kga-2) was also estimated as it was the dominant mineral component in these two soils. The method similar to that of Marcano-Martinez and McBride (1989) and Schofield (1949) was employed as described in the Ion adsorption section of Chapter 3 (pg. 30). The Mollisol was not included as it was composed predominantly of permanent charge material (Table 4-1) and has little pH-dependent charge.

Statistics

The SAS program (SAS Institute, 1996) was used to calculate the means and least significant differences ($p < 0.01$) between the amounts of Cd or Pb sorbed for various treatments in different soils.

Results and Discussion

Sorption Isotherms as a Function of Initial Cd and Pb Concentration

Sorption isotherms of Cd and Pb were constructed to compare metal sorption capacity between different soils and metals (Fig. 4-1). Lead sorption > Cd sorption in the Oxisol and Ultisol samples at initial metal concentration of > 0.1 m*M* ($p < 0.01$). The

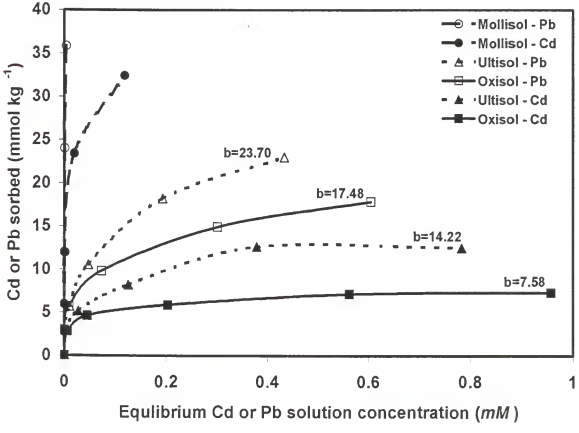

Figure 4-1. Cadmium and Pb sorption isotherms (I = 0.01 M $NaNO_3$); b is the sorption maximum as determined by the linear form of the Langmuir equation in units of mmol kg^{-1}. Ultisol and Oxisol, $R^2_{Pb\ \&\ Cd} = 0.99$.

Mollisol sample sorbed roughly equal amounts of Cd and Pb up to an initial metal concentration of 0.4 m*M* ($p \geq 0.8$). This type of sorption behavior is typical of Mollisols and other temperate region soils (Hooda and Alloway, 1994; Hooda and Alloway, 1998) due in part to their mineralogy (yielding a higher CEC), higher pH, and generally greater amount of sorption sites compared to highly weathered tropical soils (McBride, 1994; Table 4-1).

The preference exhibited by these soils for Pb over Cd (Fig. 4-1) has been observed by others (Gao et al., 1997; Pardo, 2000; Phillips, 1999) and may be attributed to Pb's smaller hydrated radius (Pb^{2+} = 0.401 nm; Cd^{2+} = 0.426 nm; Nightingale, 1959); the greater affinity of Pb for most functional groups in organic matter, which are hard Lewis bases - carboxylic and phenolic groups (Pb^{2+} is a borderline hard Lewis acid while Cd^{2+} is a soft Lewis acid); as well as its higher electronegativity (2.10 and 1.69 for Pb and Cd, respectively) and pK_H (negative log of hydrolysis constant; 7.78 and 11.70 for Pb and Cd, respectively), making it a better candidate than Cd for electrostatic and inner-sphere surface complexation reactions (Huheey, 1983; McBride, 1994).

At the maximum initial metal concentration (1.2 m*M*), the Oxisol and Ultisol soils exhibited sorption maxima (L-type sorption), as determined by the linearized form of the Langmuir equation (Eq. 4-1), for both metals while the Mollisol (H-type sorption) did not. However, in the latter soil, the sorption isotherm for Cd began to bend at the two highest initial metal concentrations (0.8 and 1.2 m*M*) suggesting an approach toward a sorption maximum. This was not evident when Pb was added at the same concentrations.

$$C/(x/m) = 1/(kb) + C/b \qquad [4\text{-}1]$$

The equilibrium solution metal concentration (m*M*) is given by C, x/m is the amount of metal sorbed in mmol kg^{-1} of soil, b is the sorption maximum (mmol kg^{-1}), and k is a constant relating to the binding energy of Cd or Pb to the soil.

Metal sorption followed the general trend of Mollisol > Ultisol > Oxisol and Pb > Cd (significantly different at $p < 0.01$ at metal concentrations of 0.8 and 1.2 m*M*). The trends reflected the differences in soil clay mineralogy and CEC but were contrary to the clay quantity and BET surface area values for these three soils (Table 4-1). The Mollisol contained the highest amount of permanent charge minerals and had the highest CEC but the lowest clay content and BET surface area among the three soils. The Oxisol, had a high clay content and the highest relative surface area, consisted exclusively of variable charge materials (1:1 phyllosilicates, Fe/Al oxides, and organic matter) and had the lowest CEC of the 3 soils. Therefore, in our soils, metal sorption was more dependent on clay type than amount of clay. BET surface area was not a good predictor of the soils' ability to sorb metals because this technique only determines external surface area. Also, the data suggest that if organic matter was the critical factor in metal sorption in these soils, the Oxisol would have sorbed the greatest amount of metals as it contained the most organic matter of the three soils. As this was not the case, the inorganic colloidal fraction appeared to be the dominant sorbent for the two metals. This is consistent with results obtained by Hanafi and Sjiaola (1998) for Cd and Zn sorption in tropical soils from Malaysia.

Sorption of Cd and Pb as a Function of pH

Soil pH plays a major role in the sorption of heavy metals as it directly controls the solubilities of metal hydroxides, as well as metal carbonates and phosphates. Soil pH also affects metal hydrolysis, ion-pair formation, organic matter solubility, as well as surface charge of iron and aluminum oxides, organic matter, and clay edges (Bruemmer et al., 1986; McBride, 1994; Sauve et al., 1998a; Sauve et al., 1998b). Increasing soil pH increases cationic heavy metal retention to soil surfaces via adsorption, inner-sphere surface complexation, or precipitation and multinuclear type reactions (McBride, 1994; Sparks, 1995). This phenomena has been demonstrated by many researchers in a variety of temperate region soils and soil mineral analogs in both batch and column studies (Altin et al., 1999; Basta et al., 1993; Kinneburgh et al., 1976; Rose and Bianchi-Mosquera, 1993; Yong and Phadungchewit, 1993).

Soil sorption of Cd and Pb in our experiment followed the expected trend of increased metal sorption with increased soil pH (Fig. 4-2). The pH_{50} values (pH at 50 % metal sorption; Kinneburgh et al., 1976) followed a similar trend as those found for the isotherm study - Mollisol-Pb (2.45, linear interpolation) << Mollisol-Cd (3.55) < Ultisol-Pb (3.62) < Oxisol-Pb (4.00) < Ultisol-Cd (4.60) < Oxisol-Cd (4.92). The only significant differences ($p < 0.01$) in pH_{50} values, within a soil order, were those found for Mollisol-Pb and Mollisol-Cd. Within a soil type, Pb had lower pH_{50} values than Cd, which is similar to results published by Kinneburgh et al. (1976) for Fe and Al oxides.

Data in Fig. 4-2a identified regions along the pH continuum where sorption behavior was most affected by pH (sorption envelope), and other areas where sorption increased less ($\Delta pH \approx 1$ resulted in Δ% sorbed ≤ 8 %). Furthermore, in the sorption

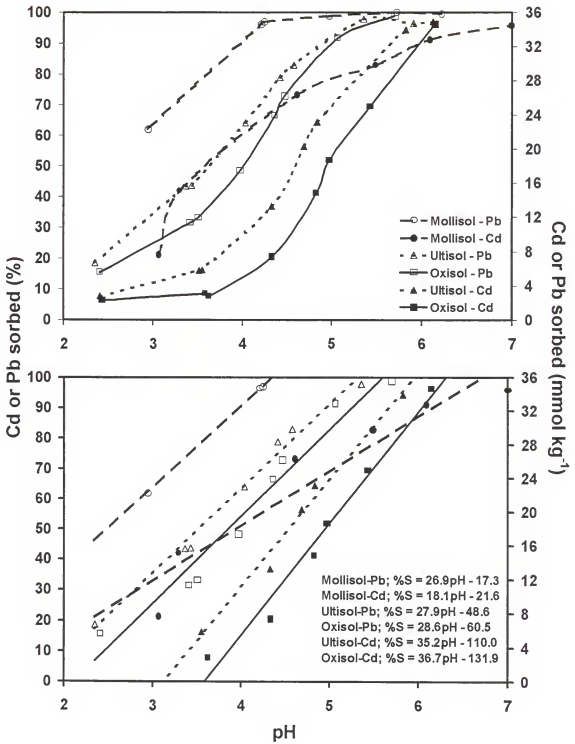
Cd or Pb sorbed (%)
Cd or Pb sorbed (mmol kg-1)
pH
Mollisol - Pb
Mollisol - Cd
Ultisol - Pb
Oxisol - Pb
Ultisol - Cd
Oxisol - Cd
Mollisol-Pb; %S = 26.9pH - 17.3
Mollisol-Cd; %S = 18.1pH - 21.6
Ultisol-Pb; %S = 27.9pH - 48.6
Oxisol-Pb; %S = 28.6pH - 60.5
Ultisol-Cd; %S = 35.2pH - 110.0
Oxisol-Cd; %S = 36.7pH - 131.9

Figure 4-2. Cadmium and Pb (a) sorption as a function of pH ($I = 0.01\ M\ NaNO_3$) and (b) sorption envelopes of Cd and Pb using a linear model ($R^2 > 0.91$). Points where Δ% sorbed ≤ 8 % when $\Delta pH \approx 1$ were omitted ($I = 0.01\ M\ NaNO_3$; %S = % sorbed).

envelope the slopes of the sorption curves appeared to be similar. Therefore, in the low sorption areas (as defined above), the data points were removed and straight lines were fit to the remaining data yielding lines with $R^2 \geq 0.91$ (Fig. 4-2b).

Slopes of the lines (excluding Mollisol-Cd data) suggest that metal sorption depended more on metal type than on soil components (Fig. 4-2b). The slopes of the Pb sorption curves were similar and within ± 1 unit of each other, whereas those of Cd had slightly more variability. A unit increase in pH resulted in ≈ 28 % and 36 % (avg. of Oxisol and Ultisol values, respectively) increase in Pb and Cd sorption, respectively. Therefore, Cd sorption occurred over a narrower pH range than Pb regardless of soil composition. This behavior can be attributed to a greater tendency of Pb to undergo both inner- and outer-sphere surface reactions than Cd over a wide pH range. An anomaly to the above generalization was the Mollisol-Cd line, which exhibited the lowest slope of all soil-metal lines (≈ one-half that of the Oxisol-Cd and Ultisol-Cd lines). This was indicative of sorption phenomena occurring over a larger pH range compared to the other soils (Fig. 4-2).

Cadmium(II) is a closed shell cation (valence orbital is full – d^{10}) that favors coulombic type reactions (Huheey, 1983) at soil surfaces as opposed to inner-sphere surface reactions (electron sharing). Thus, Cd sorption should increase more than Pb sorption with increases in soil CEC. Hanafi and Sjiaola (1998) observed that CEC was highly positively correlated ($r = 0.89$) to the sorption of Cd^{2+} and Zn^{2+} (d^{10} cations) in acid tropical soils. Naidu et al. (1997) found Cd sorption to depend strongly on surface charge density in tropical soils while Zachara et al. (1992) found that sorption of Cd on

the edges of layer silicates and on Fe and Al oxides was controlled by the CEC (at pH < 6.5).

Surface charge on the Mollisol predominantly originated from minerals with constant surface charge (Table 4-1). Its negative surface charge density should not have increased much over the pH range of this experiment (≈ 2 to 7) compared to the Oxisol and Ultisol. Thus, the Mollisol-Cd curve had a relatively flat slope (≈ 18 units) compared to the sorption curves of the other soils (Fig. 4-2b). Yong and Phadungchewit (1993) reported similar sorption behavior for Cd on montmorillonite; metal sorption occurred over a wider pH range on montmorillonite than on kaolinite or illite. They also observed lower pH_{50} values for Pb than Cd in clayey soils ($\Delta pH_{50} \approx 2$ units). In contrast to the Mollisol, the Oxisol and Ultisol soils in our study were predominantly composed of minerals with variable-charge (Table 4-1). These two latter soils displayed great increases in negative surface charge with increasing pH (Fig. 4-3). It follows that the sorption curves of these soils had steeper slopes of Cd sorption as a function of pH (≈ 36 units) than in the Mollisol soil. Naidu et al. (1994) also reported steep sorption isotherms for Cd in two Oxisols with increasing pH.

Surface Charge and Cd and Pb Sorption

Comparing the amount of negative surface charge to the amount of sorbed Cd^{2+} or Pb^{2+} ($mmol_c\ kg^{-1}$), as a function of pH, yielded information regarding the nature of the reactions occurring on the surfaces of the Oxisol and Ultisol soils. The PZNC values of the Ultisol and Oxisol were ≈ 2.3 and 3.7, respectively. At pH values below the PZNC, the soil surfaces had net positive charge and would, therefore, be prone to

electrostatically repel cations. The Oxisol retained metals below its PZNC, whereas sorption curves are above zero (≥ 5 $mmol_c$ kg^{-1}) at pH < 2.5 (Fig. 4-2a) for the Ultisol. As cation retention would not be favored when the soil surfaces contained net positive charge, this sorption behavior could be indicative of inner-sphere surface complexation or adsorption to sites possessing some negative charge (e.g. permanent charge sites such as vermiculite, smectite, and/or organic matter).

Figure 4-3 further elucidates the nature of the metal surface interactions by presenting the relationship between pH and the amount of sorbed Cd^{2+} or Pb^{2+} (expressed in equivalents) and the negative surface charge determined from adsorption of Na^{+}. In most cases, the Ultisol had more negative surface charge at a given pH than the amount of either Cd^{2+} or Pb^{2+} sorbed. An exception may possibly be found for the sorption of Pb at pH $\leq$ 2.6, where the surface charge and Pb sorption curves intersect (Fig. 4-3a), but, the data are inconclusive. Yong and Phadungchewit (1993) observed Pb sorption at pH < 2 in several clayey soils that retained much less Cu, Zn, and Cd at about the same pH values. We suggest that the sorption reactions were mainly non-specific (electrostatic) at low pH, with some evidence of specific inner-sphere surface complexation of Pb at pH $\leq$ 2.6. However, oxide solubility and the 0.01 background *I* become highly dependent on pH at these low values (< 2.5), thus, ascertaining modes of metal sorption with any certainty becomes difficult.

The amount of Pb sorbed by the Oxisol, at any pH, was well above the amount of negative surface charge (>10 $mmol_c$ kg^{-1}). The amount of Cd sorbed closely mirrored the quantity of negative surface charge up to the PZNC (Fig. 4-3b). The data suggests both inner- and outer-sphere reactions of Pb with the soil surface, whereas Cd likely sorbs to

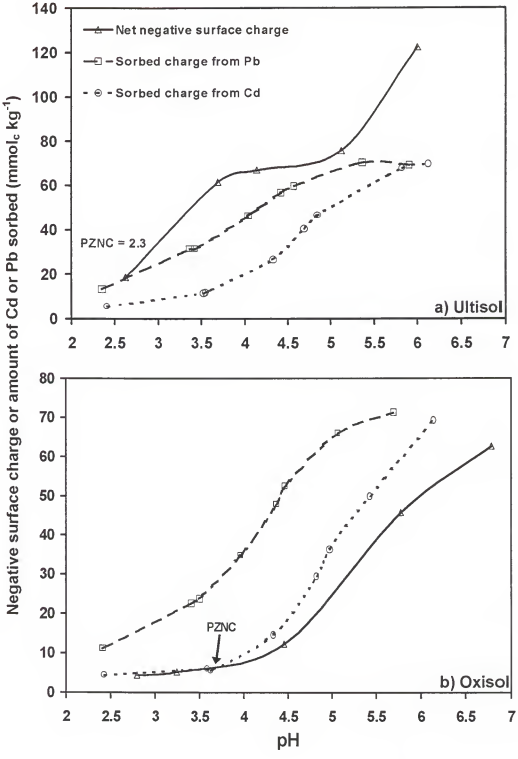

Fig 4-3. Relationship between the amount of sorbed Cd or Pb and the amount of negative surface charge for the (a) Ultisol and (b) Oxisol as a function of pH (I = 0.01 M $NaNO_3$ or NaCl). Complete sorption of added Cd or Pb corresponds to 72 meq cation kg^{-1}.

exchange sites. However, above pH ≈ 3.7, the amount of Cd sorbed exceeded the CEC, which may suggest inner-sphere surface complexation.

Soil solutions were undersaturated with respect to solid formation of $Cd(OH)_2$ and $Pb(OH)_2$ as well as $CdCO_3$ and $PbCO_3$ ($P_{CO_2} = 10^{-3.5}$ atm). Furthermore, when matrix blanks [solutions containing $NaNO_3$ + $Cd(NO_3)_2$ or $Pb(NO_3)_2$] were titrated with base, no solid phase was formed in the presence of Cd in the pH range of the experiment. However, there was evidence for $Pb(OH)_2$ (s) only at pH ≥ 5.9. Fig. 4-3 shows that the highest pH values in experiments involving Pb were 5.9 and 5.7 for the Ultisol and Oxisol, respectively. Thus, solid phase precipitation can generally be ruled out as a retention mechanism here.

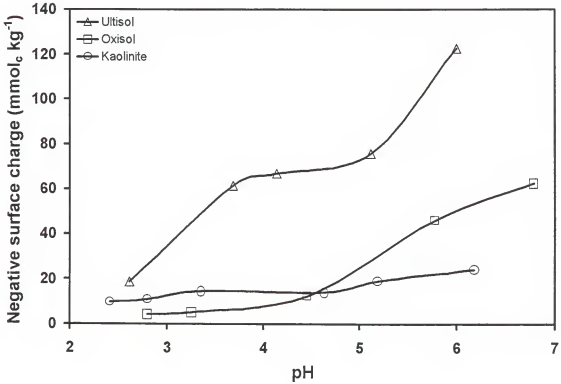

Figure 4-4. Relationship between the negative surface charge and pH (I = 0.01 M NaCl). Complete sorption of added Cd or Pb corresponds to 72 meq cation kg^{-1}.

Regarding the negative surface charge curve for the Ultisol (Fig. 4-3a), we noticed the negative surface charge appeared to be buffered between pH values ≈ 3.7 to 4.7 (relatively flat slope) while the Oxisol (Fig. 4-3b) did not exhibit such behavior. Upon comparing the negative surface charge curves for these soils and kaolinite as a function of pH, we noticed similarities only in the shapes of the Ultisol and kaolinite curves (Fig. 4-4). This was surprising in that both soils were dominated by kaolinite in the clay mineral fractions (≈ 45 and 49 %, respectively for the Ultisol and Oxisol soils). However, the Oxisol contained over twice as much organic matter as the Ultisol (Table 4-1), which most likely overshadowed kaolinite's buffering capacity as was witnessed for the latter soil in the pH range 3.7 to 4.7.

Conclusions

Experiments conducted on the sorption of Cd and Pb in tropical soils from Puerto Rico indicated greater affinity of Pb for soil sorption sites than Cd. The sorption maxima (estimated from the linearized Langmuir equation) were greater (≈ 10 mmol kg^{-1}) for Pb than for Cd in the Oxisol and Ultisol. The Mollisol failed to demonstrate a sorption maximum for either metal as the treatment concentrations in our experiment (0 to 1.2 m*M* metal) were not high enough to show this behavior. This soil exhibited a preference for Pb over Cd. Metal sorption as a function of pH yielded similar results, where pH_{50} values increased in the order; Mollisol-Pb < Mollisol-Cd < Ultisol-Pb < Oxisol-Pb < Ultisol-Cd < Oxisol-Cd. These trends are in agreement with soil CEC variation and inversely related to soil organic matter contents, clay contents, and BET surface areas. Soil clay mineralogy, specifically the presence of 2:1 permanent charge minerals, was more

important for Cd and Pb sorption than the quantity of organic matter and the external surface area in these soils.

Within the sorption envelopes ($\Delta pH \approx 1$ resulted in $\Delta\%$ sorbed > 8 %), Cd sorption curves had similar slopes across all soils (excluding Mollisol-Cd) as did the Pb sorption curves for each of the soils. Straight lines were fit to the data yielding $R^2 \geq 0.91$ and slopes of 28±1 and 36±1 % increase in Pb or Cd sorption per 1 unit increase in pH, respectively. We conclude that metal type is more important than soil composition for the sorption of either Cd or Pb in our soils. Furthermore, pH had a larger effect on Cd sorption than on Pb sorption.

Plots of negative surface charge and sorbed Cd or Pb (Oxisol and Ultisol only) vs. soil pH were used to suggest possible sorption mechanisms (outer- vs. inner-sphere). Both soils likely sorbed Cd electrostatically in the low pH ranges (< 4) and possibly through inner- and outer-sphere reactions above pH 4. This was especially important for the Oxisol. The amount of Cd sorbed, in equivalents, balanced the amount of negative surface charge up to this soil's PZNC (3.7). In both soils, at pH > 4, the negative surface charge was similar to or greater than the amount of sorbed Cd. The amount of Pb sorbed, on the other hand, was much larger (≥ 10 $mmol_c$ kg^{-1}) than the amount of negative surface charge throughout the pH range (2.5 to 6.5) for the Oxisol, suggesting both inner- and outer-sphere reactions. Evidence for inner-sphere reactions of Pb and the Ultisol surface sorption sites, especially at pH < 2.6, was inconclusive.

Lead demonstrated a higher affinity for tropical soil sorption sites relative to Cd. The former metal also confirmed its tendency to take part in inner-sphere surface reactions (especially at pH < PZNC). Lead was much less bioavailable and mobile in our

tropical soil systems than Cd. Therefore, it poses much less of a threat of contaminating underlying groundwater, compared to Cd.

Many times a metal contaminated site may receive inputs of one metal before another. For example, a site contaminated with Cd from smelting operations may later receive large quantities of Pb if it became an automobile battery reclamation facility. In order to supplement the knowledge gained from the studies of this chapter, it will be interesting to look at how Cd and Pb react when introduced to tropical soils together and sequentially (i.e. one after the other).

CHAPTER 5
SEQUENTIAL SORPTION OF Pb AND Cd IN THREE TROPICAL SOILS

Introduction

Cadmium and Pb are used in many industrial, urban, and agricultural applications (Adriano, 1986; U.S. EPA, 1992; Kabata-Pendias and Pendias, 1992) and are often found together at heavy metal contaminated sites. Locations receiving incinerator fly-ash (Lim et al., 1997; Roy et al., 1993), high levels of biosolids (Hooda and Alloway, 1994; Sloan et al., 1997), scrap iron/metal (Jensen et al., 2000), and areas surrounding Pb-Zn mines and Al smelters (Merrington and Alloway, 1994; Merrington and Alloway, 1997; Wilcke et al., 1998b) have been shown to contain high amounts of these two soil contaminants. Therefore, understanding the chemistry of Cd and Pb interactions, under a variety of reaction conditions, in the soil environment is of great importance in the consideration of possible remediation strategies.

Heterogeneous soil systems are composed of a variety of organic and inorganic constituents which have differing affinities for heavy metals. These differences are predominantly a function of the dominant types of soil surfaces present as well as the metals existing in the soil system. In addition, the heavy metals themselves exhibit varying affinities for soil surfaces. For example, Pb and Cu are strongly sorbed to soil surfaces while Cd and Zn generally have lower affinities for sorption sites. The variability in heavy metal affinity for soil sorption sites has been attributed to a particular

metal's hydrolysis constant (pK_H), electronegativity, Lewis acidity, solubility (K_{SP}) of precipitates such as those involving hydroxide and carbonate, and charge density (size and charge) (McBride, 1994; Pardo, 2000; Phillips, 1999; Yong and Phadungchewit, 1993).

A contaminated site may receive doses of these metals at varying times. For example, soils at battery recycling centers may get high quantities of Pb from car batteries at one time and then later receive inputs of Cd from domestic batteries. Understanding how particular metals interact and may compete for soil sorption sites when entering a soil system at different times is of great interest. Also, ascertaining the mechanism of the heavy metal-soil surface reactions is helpful as it sheds light on the strength and stability of the surface complex formed.

Most research has focussed on the interactions of certain heavy metals added together to temperate region soils and/or soil components. Several researchers (Echeverria et al., 1998; Gao et al., 1997; Kinneburgh et al., 1976; Phillips, 1999; Yong and Phadungchewit, 1993) found Pb was retained more than Cd when these metals were added simultaneously to soils and pure mineral systems. In contrast, relatively few studies have dealt with the competitive sorption reactions involving heavy metals and tropical soil. No known research has looked into reactions of Cd and Pb in soils when these two metals are added in a sequential reaction scheme (Fig. 5-1).

Pertinent and useful information as to how these cations are sorbed to soil surfaces may be ascertained via determination of the relative proportion of the sorbed heavy metal which is exchangeable versus that which is retained by soil solids (e.g. non-specifically sorbed and specifically sorbed, respectively; Tiller et al., 1984b).

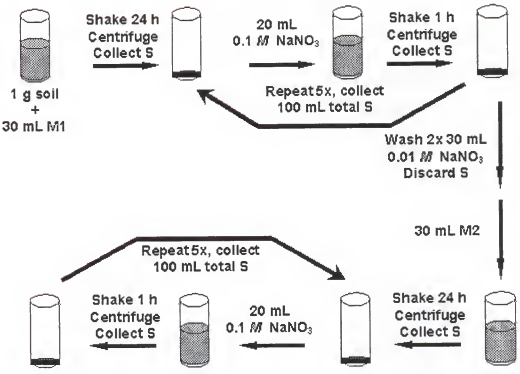

Figure 5-1. Sequential addition scheme of Pb and Cd to soils. S = supernatant.

Sorption/desorption studies generally employ the use of a neutral salt solution ($Ca(NO_3)_2$, $CaCl_2$, $NaNO_3$, etc.) to desorb previously sorbed metals from soils or mineral components. This enables the researcher to ascertain the fraction of the sorbed metal which was non-exchangeable and, thus, sorbed at high affinity sites. In most cases, studies considering the sorption/desorption of Cd and Pb have indicated the latter metal to be much less desorbable than the former (Hansen and Maya, 1997; Pardo, 2000). However, Ainsworth et al. (1994) found Cd desorption was less than that of Pb at pH 3 on aged hydrous iron oxide. It was suggested this to be most likely due to the

incorporation of Cd and not Pb (sorption completely reversible) into the iron oxide structure.

Sequential extraction procedures have also been employed to assess the relative affinities of both Cd and Pb to various soil fractions (exchangeable, carbonate bound, Fe and/or Mn oxide bound, etc.; Tessier et al., 1979). In several studies reviewed, more Cd was always found in the exchangeable fraction compared to Pb in soils where heavy metals were added (Majone et al., 1998; Salim et al., 1996) or applied via fly ash (Lim et al., 1997) or biosolids amendments (Sloan et al., 1997).

The above studies, and others like them, have yielded valuable information regarding the interactions of Cd and Pb with soil and mineral surfaces (i.e. reversible vs. irreversible sorption). However, further important information, particularly the interaction of the above metals with each other and the specificity of sorption sites for one metal species over another, can be obtained by employing a modified approach to the traditional sorption/desorption and/or sequential extraction procedures.

Figure 5-1 displays our modified sequential reaction scheme. First, soils are equilibrated with either Cd or Pb. Second, the sorbed metal from the first step is exchanged with Na. Third, a new addition of either Cd or Pb (whichever one was not added in the first step) is made and equilibrated with the soil. Fourth, this second addition of Cd or Pb is then exchanged with Na. Employing such an approach enables the experimenter to ascertain the extent to which soil sorption sites are metal specific, determine the nature of heavy metal-soil surface reactions (e.g. non-specific or electrostatic v. specific or surface complex formation; Tiller et al., 1984b), as well as

identify how metals will compete for sorption sites when they enter soil systems at different times.

No published research to date has dealt with the questions of sorption mechanisms and ion interactions when Cd and Pb are added to tropical soils in a sequential reaction scheme (Fig. 5-1). The objectives of this research were to investigate how adding the above metals sequentially to three tropical soils from Puerto Rico affects their i) retention, ii) modes of sorption, and iii) competition for sorption sites.

Materials and Methods

Materials

The A-horizons (≈ 0 - 15 cm) of the three Puerto Rican tropical soils (Mollisol, Oxisol, and Ultisol) were used in this study. Table 4-1 (pg. 50) presents pertinent physicochemical properties of the soils, found using standard procedures, used in this study.

Determination of Cd and Pb Sorption

All soils were passed through a 0.5 mm sieve and air-dried. All metal analyses were done on a flame atomic absorption spectrophotometer (AAS) on unfiltered samples as preliminary experiments showed no significant differences between metal concentrations in samples which were filtered through 0.45 μm Millipore filters and those which were not. Finally, each treatment was replicated five times.

Sequential Addition of Metals

Lead, Cd, Pb + Ca, Cd + Ca, and Pb + Cd were added to the soils, which were Na-saturated, in order to determine the extent to which these metals compete for sorption sites, their mechanisms of sorption (e.g. sorption to high affinity vs. exchange sites), and to ascertain the effect of adding the metals sequentially to the different soils. The experiments were comprised of 5 sequences. Each sequence had a different order of metal addition. For example, in Sequence 1, Pb was equilibrated with the soils first followed by Cd. The order of metal addition in Sequence 2 was exactly the opposite of Sequence 1 (Table 5-1).

Table 5-1. Sequential addition of Pb and Cd to soils.

Sequence #	1st metal/s added (M1)	[M1]†	2nd metal added (M2)	[M2]
1	Pb	1.2	Cd	1.2
2	Cd	1.2	Pb	1.2
3	Pb + Ca	1.2 each	Cd	1.2
4	Cd + Ca	1.2 each	Pb	1.2
5	Pb + Cd	1.2 each	none	na

†Brackets indicate concentrations in mmoles L^{-1}.

Figure 5-1 provides a schematic flowchart of how the procedure was performed. Using Sequence 1 as an example (Table 5-1), 30 mL of 1.2 m*M* $Pb(NO_3)_2$ (M1), in $NaNO_3$ background electrolyte (*I* of solution = 0.01 *M*), was added to ≈ 1 g soil in a pre-weighed 50 mL centrifuge tube. The suspension was then equilibrated on a reciprocating shaker for 24 h at 25 ± 3°C. Preliminary kinetic studies indicated a 24 h reaction period was sufficient to achieve equilibrium conditions when using a reciprocating shaker.

The sample was centrifuged and the supernatant collected for later analysis of the amount of Pb (M1) sorbed, which was determined by difference, on the flame AAS. The adsorbed Pb (M1) was then displaced by 5 washings with 20 mL aliquots of 0.1 *M* $NaNO_3$ with shaking for 1 h between washes. Extracts were combined and stored in a refrigerator (4° C) prior to analysis of exchangeable Pb (E1) on the flame AAS (E1 concentration was corrected for occluded E1). The amount of adsorbed Pb not exchanged by the $NaNO_3$ washes was operationally defined as being specifically sorbed Pb or Pb sorbed to high affinity sites (Tiller et al., 1984b). The *I* of the soil solutions was readjusted to it's original value via two 30 mL washes with 0.01 *M* $NaNO_3$, shaking for 1 h between each rinse.

The supernatant was discarded and 30 mL of 1.2 m*M* $Cd(NO_3)_2$ (M2), in $NaNO_3$ background electrolyte, was added to the soil and shaken for 24 h at 25 ± 3°C on a reciprocating shaker. The samples was centrifuged and the supernatant collected and refrigerated (4° C) for later analysis of the amount of sorbed Cd (M2), which was found by difference, as well as any Cd (M2) replaceable Pb (M1). The soils were again washed 5 times with 0.1 *M* $NaNO_3$, shaking for 1 h between each wash, to remove adsorbed Cd (M2). The extracts were combined and stored in a refrigerator (4° C) prior to analysis of exchangeable Cd (E2) on the flame AAS (E2 concentration was corrected for occluded E2). As before, any adsorbed Cd (M2) remaining was operationally defined as specifically sorbed Cd or Cd sorbed to high affinity sites (Tiller et al., 1984b).

Prior to the initiation of this experiment, a rather rigorous soil pre-treatment was necessary to insure the differences in metal sorption (e.g. Pb and Cd) were due to differences in the metals' affinity for sorption sites. Preliminary data showed a

systematic increase in sorption of M2 for all soils. This was postulated to be a result of physical breakdown of the soil, due to shaking, resulting in increased metal exposure to sorption sites. The hypothesis was confirmed when Cd was added in the M1 and M2 positions and sorption of M2 > M1. In order to offset this effect, all soils underwent cation exchange reactions where 0.1 *M* KNO_3 and 0.1 *M* $NaNO_3$ were added in an alternating fashion until a constant CEC was obtained.

Specifically, the soils were shaken for 1 h at 25 ± 3°C with one of the above solutions, centrifuged with supernatant collection and refrigeration (4° C), and followed by addition of the other solution. The soils were then re-suspended and the procedure repeated. Concentrations of adsorbed K or Na were determined on the flame AAS.

Statistical Methods

Least squares means significant differences ($p \leq 0.01$) were calculated with the SAS program (SAS Institute, 1996) between the amounts of metal sorbed, exchanged, or replaced for various treatments and soils.

Results and Discussion

Effect of Sequence of Metal Addition

Sequence of a metal addition had little influence on the extent to which Pb was retained in the Oxisol, Ultisol, or Mollisol soils. All differences between sorbed Pb (M1 v. M2) and exchanged Pb (E1 v. E2), when this metal was added to the soils before Cd as compared to when it was introduced to the soils after Cd, were insignificant (Fig. 5-2). However, this same phenomenon was only observed for the differences between sorbed

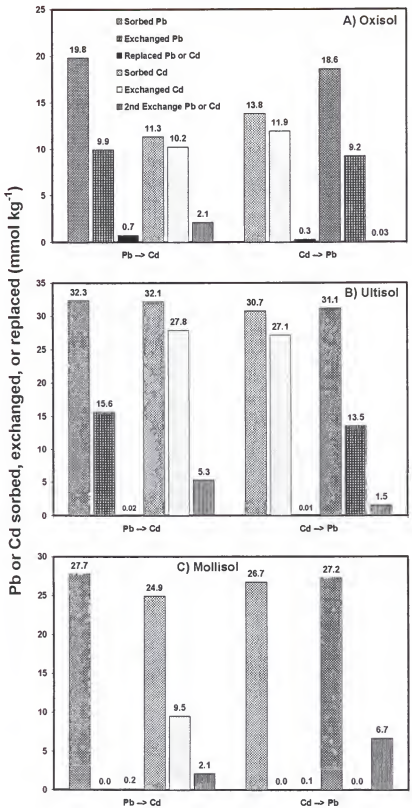

Figure 5-2. Monometal sequential addition of Pb → Cd (Sequence 1) and Cd → Pb (Sequence 2) to A) Oxisol, B) Ultisol, and C) Mollisol.

Cd (M1 v. M2) and exchanged Cd (E1 v. E2) in the Ultisol. The Oxisol showed a significant ($p = 0.01$) increase in the amount of sorbed Cd (13.8 mmol kg^{-1}) when this metal was introduced to the soil prior to Pb (M1) as opposed to when it entered this soil system after Pb (M2; sorbed Cd = 10.2 mmol kg^{-1}; Fig. 5-2a). Also, Cd had no appreciable exchangeable fraction when it was introduced to the Mollisol before Pb while 38 % (Fig. 5-2c) sorbed Cd was exchangeable when it was added to the Mollisol after Pb. Therefore, if Pb is introduced to these soils prior to Cd, it has the ability to inhibit the sorption of Cd to both exchange and high affinity sorption sites but not vice-versa. This finding is consistent with data presented by Salim et al. (1996).

After a metal was exchanged by Na, little (≤ 0.7 mmol kg^{-1}) Pb was replaced by Cd and even less Cd (≤ 0.3 mmol kg^{-1}) was replaced by Pb in all soils (Figs. 5-2 and 5-3). Thus, neither of the metals effectively replaced the other from high affinity sorption sites. However, all soils (especially the Mollisol in Sequence 4) in Sequences 1-4 exchanged additional amounts of the metal added in the M1 position after going through the entire reaction schemes (2^{nd} exchange M). For example, the Oxisol (Fig. 5-2a, Sequence 1) originally sorbed 19.8 mmol kg^{-1} Pb of which 50 % was exchangeable and 4 % of the remaining Pb was later replaced by Cd. Of the Cd added, the soil sorbed 11.3 mmol kg^{-1} most of which was exchanged by Na (90 %). This second Na extraction replaced another 2.1 mmol kg^{-1}, or 23 % of the remaining sorbed Pb which was previously unexchangeable by Na and unreplaceable by Cd, into solution.

The explanation does not appear to be a question of reaction kinetics as most ion exchange processes occur on micro to millisecond time scales (Sparks, 1999). Furthermore, the amounts of replaceable metal were very low, ≤ 4 % of the remaining

sorbed metal after exchange, and in most cases much less than what was previously exchanged by Na. This was indicative of complete exchange of the exchangeable fraction by Na.

The possibility exists that the systems were in states of disequilibrium. Under this hypothesis, metal initially present as an irreversibly sorbed phase (i.e. nonexchangeable and nonreplaceable) had a tendency to shift from high affinity sites to ones of lower affinity (exchangeable) to maintain an equilibrium amount of metal on the high and low affinity sorption sites. This may have occurred as the first exchangeable fraction was decanted/removed prior to addition of the next metal.

In studies performed by Strawn (1998) and Strawn et al. (1998), Pb was shown to be completely desorbed within several days in montmorillonite and Al_2O_3 systems. In these studies, the desorbed phase was continually removed from the reaction vessel. Gunneriusson (1994) and Gunneriusson et al. (1994) saw complete reversibility of sorbed Pb and Cd on goethite. In the above studies, inner-sphere complexes were shown to form in the original sorbed phases by either EXAFS (Extended X-ray Absorption Fine Structure Spectroscopy) or the Constant Capacitance Model. However, in soil, Strawn and Sparks (2000) found from 32 % to 76 % Pb was desorbed (within $\approx$ 240 min).

Mechanisms of Metal Sorption

Contrary to the other two soils, the Oxisol had sorption maxima that changed little (range $\approx$ 3 mmol kg^{-1}) for single (Fig. 5-2) and composite (Pb + Ca and Pb + Cd; Figs. 5-3 and 5-4a and b) additions of Pb denoting saturation of sorption sites at $\approx 19.4 \pm 1.5$ mmol kg^{-1} (avg. of 5 values). In all cases, this soil sorbed concentrations of Pb exceeding

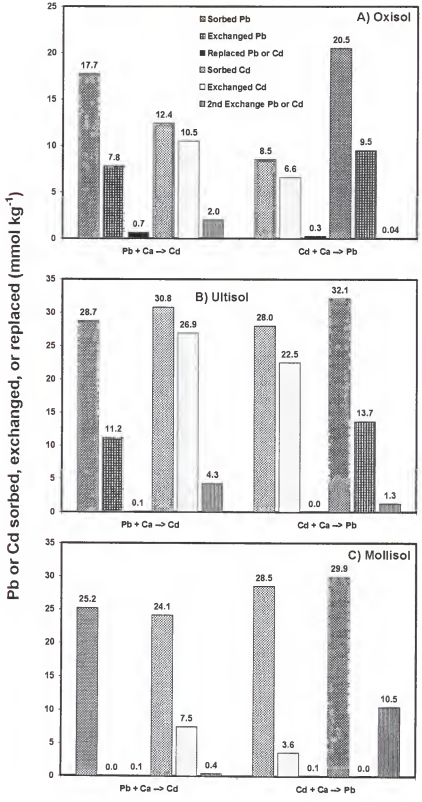

Figure 5-3. Bimetal additions of Pb + Ca → Cd (Sequence 3) and Cd + Ca → Pb (Sequence 4) in A) Oxisol, B) Ultisol, and C) Mollisol.

its CEC while the greatest quantity of sorbed Cd was ≈ 88 % of the Oxisol's CEC of 3.1 $cmol_c\ kg^{-1}$ (Table 4-1; pg. 50).

On the other hand, the amounts of metals sorbed (Pb, Cd, and Ca monometal or composite additions) by the Ultisol or Mollisol never exceeded their CEC values of 11.0 and 20.9 $cmol_c\ kg^{-1}$, respectively (Table 4-1; pg. 50). This presents a strong case for the sorption of Pb via inner-sphere and electrostatic sorption mechanisms and Cd by mainly exchange reactions in the Oxisol. However, the CEC data, by itself, did not yield conclusive information for metal sorption mechanisms occurring in the Ultisol or Mollisol.

Information regarding the modes of metal sorption in our soils (especially Ultisol and Mollisol) was obtained by looking at the exchangeable Pb or Cd fractions. In each of the soils, we noticed the sorbed and exchanged amounts of a particular metal were approximately equal (e.g. Pb sorbed in position M1 = Pb sorbed in position M2; $p >$ 0.01), within a soil type, in Sequences 1 and 2 (Fig. 5-2; Oxisol-Cd M1 v. M2 and Mollisol-Cd E1 v. E2 excepted). Less than half of the initially sorbed Pb was exchangeable while, in most cases, ≥ 80 % initially sorbed Cd was exchanged (Mollisol excepted; Figs. 5-2 to 5-4). This indicated Pb had a greater tendency to be sorbed at high affinity sorption sites relative to Cd in our soils.

Tiller et al. (1984b) used a similar method to partition sorbed Cd, Ni, and Zn between high affinity/specific sorption sites and lower affinity/exchange sites. They described the sorbed metal fraction that was retained by soils after 0.01 *M* $Ca(NO_3)_2$ washes as being specifically sorbed or sorbed at high affinity sorption sites. The exchangeable fraction was deemed to have been sorbed at lower affinity sites.

As ascertained by x-ray absorption spectroscopy such as EXAFS and XANES (X-ray Absorption Near Edge Structure Spectroscopy), the pertinent mechanism of inner-sphere complexation of a metal (M) to a soil surface (e.g. goethite, gibbsite, organic matter) usually involves formation of covalent bond/s between the metal and an oxygen (O) originating from a soil surface. The oxygen may be from an organic (Xia et al., 1997a, b) or inorganic (Scheidegger et al., 1996, 1998; Strawn et al., 1998) surface functional group.

In layer silicates, however, generally regarded as exchangers, irreversible or non-exchangeable metal sorption may be through several mechanisms. On such materials, this reaction may occur at clay edge sites (McBride, 1989; Pardo, 2000; Strawn and Sparks, 1999; Ulrich and Degueldre, 1993; Undabeytia et al., 1998), occlusion into cavities/deformities on planar surfaces (Nakhone, 1997), and fixation in interlayer positions of 2:1 phyllosilicates. This last mechanism is only a possibility if the selectivity exhibited by the interlayer for a metal ion, Ca, Cd, and Pb in our study, is much larger than the selectivity the interlayer has for the extracting ion (Na in our study) (Sposito et al., 1983).

However, XRD confirmed Na^+ was able to replace Pb^{2+}, and presumably Cd^{2+}, from the interlayer of smectite in the Mollisol and Ultisol soils. Ceramic tiles covered with the < 2 μm fractions of these soils were saturated with Na^+, Pb^{2+}, then Na^+. The d-spacings of the smectite peaks were measured at each interval/saturation. The Na^+-saturations had similar d-spacings (14.64 Å for the Mollisol and 14.55 Å for the Ultisol) while those of Pb^{2+} were ≈ 15.03 Å (Mollisol) and 14.24 Å (Ultisol). Therefore, the

interlayer of smectite was not responsible for the irreversible sorption of Pb^{2+} (or presumably Cd^{2+}).

The Mollisol soil had a much lower exchangeable Cd fraction than the other soils. This soil sorbed nearly all the Pb and most of the Cd when these metals were added together (Fig. 5-4a). In Sequences 1-4 (Figs. 5-2 and 5-3), this soil exchanged from 0 – 38 % of originally sorbed Cd and no Pb. This was likely due to the fact that the added Cd and Pb in these sequences probably did not saturate all the available mineral and/or organic high affinity sorption sites. Thus, upon extraction with Na, nearly all the added Cd or Pb was retained by this soil (Phillips, 1999).

Pb and Cd Affinity for Soil Surfaces

Figures 5-2 to 5-4a indicated the preference the soils exhibited for Pb relative to Cd sorption regardless of the order in which Pb was added to the soils (M1 or M2). Most of the differences between sorbed Pb and sorbed Cd, within a soil type, were significant ($p > 0.01$; differences between sorbed Pb and sorbed Cd in Ultisol, Sequences 1 and 2 and Mollisol, Sequence 2 excepted). These differences in soil affinity for Pb and Cd have been observed by others in tropical soils and/or pure oxidic mineral systems (Davis and Leckie, 1978; Kinneburgh et al., 1976; Puls et al., 1991) as well as in soils low in Fe/Al oxides (Gao et al., 1997; Pardo, 2000). This is usually attributed to differences in metal characteristics and resultant affinity for sorption sites (McBride, 1994).

For example, Pb^{2+}'s hydrated radius is smaller than that of Cd^{2+} (Pb^{2+} = 0.401 nm; Cd^{2+} = 0.426 nm; Nightingale, 1959) favoring coulombic interactions of Pb over Cd with

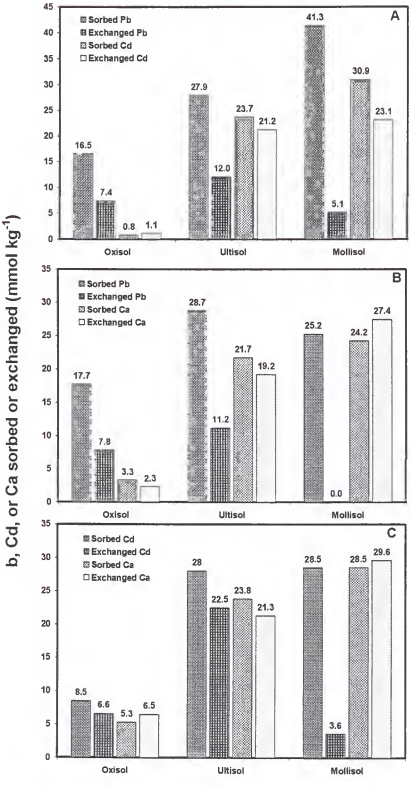

Figure 5-4. Competitive interactions between Pb, Cd, and Ca when A) Pb + Cd, B) Pb + Ca, and C) Cd + Ca were added together to the Oxisol, Ultisol, and Mollisol soils.

exchange sites. Furthermore, Pb has a greater affinity for most functional groups in organic matter, which are hard Lewis bases - carboxylic and phenolic groups (Pb^{2+} is a borderline Lewis acid while Cd^{2+} is a soft Lewis acid); a higher electronegativity (2.10 and 1.69 for Pb and Cd, respectively); and lower pK_H (negative log of hydrolysis constant; 7.78 and 11.70 for Pb and Cd, respectively) relative to Cd. This makes Pb a better candidate for inner-sphere surface complexation reactions compared to Cd (Huheey, 1983; McBride, 1994).

Lead (Pb^{2+}) has 2 valence electrons in its 6s atomic orbital which can form, depending on the Pb-O symmetry, molecular orbitals with O 2p or O 2s atomic orbitals originating from an oxide surface. This orbital overlap stabilizes the Pb-O complex. On the other hand, Cd^{2+} has a filled 4d valence atomic orbital which does not participate in electron sharing with O 2p or O 2s atomic orbitals from oxide surfaces. This disfavors formation of Cd-oxide covalent bonds relative to Pb and is consistent with the data presented in Figs. 5-2 and 5-3 as well as the above discussion on inner-sphere surface complexation reactions.

Non-Exchangeable Pb:Cd Ratios

The Oxisol and Ultisol soils, composed predominantly of 1:1 phyllosilicates and Fe/Al oxides, predominantly adsorbed Cd at exchange sites. The Mollisol clay, composed almost entirely of phyllosilicates, probably sorbed most Cd at high affinity sites of organic matter and 1:1 and 2:1 phyllosilicate minerals. The sorption of Cd by these three soils had little effect on the amount of non-exchangeable (sorbed Pb minus exchanged Pb) Pb. The non-exchangeable Pb fraction remained relatively constant

throughout all sequences in these soils ranging from 9.1 to 11 mmol kg^{-1} (Oxisol), 15.9 to 18.4 mmol kg^{-1} (Ultisol), and 25.2 to 29.2 mmol kg^{-1} (Mollisol).

In Sequences 1-4 (Figs. 5-2 and 5-3), the ratios of non-exchangeable Pb:Cd (NERs) were ≈ 6.4, 4.1, and 1.7 when Pb was added in position M1 for the Oxisol, Ultisol, and Mollisol, respectively. When Cd was added in position M1, Pb:Cd NERs were 5.4, 4.0, and 1.1 for the Oxisol, Ultisol, and Mollisol, respectively. Since the amount of non-exchangeable Pb did not change to great extent throughout these sequences, the ability of this metal to inhibit the retention of Cd at high affinity sites was demonstrated. This was because the Pb:Cd NERs were higher when Pb was added in position M1 as opposed to when Cd assumed this position. Furthermore, in Sequence 5 (Fig. 5-4a), this effect was manifested to even larger extent as the Pb:Cd NERs were ≈ 9.1, 6.4, and 4.6 for the Oxisol, Ultisol, and Mollisol respectively.

In Sequences 1-4, the Mollisol had Pb:Cd NERs near unity because this soil retained nearly equal amounts of Na-nonexchangeable Pb and Cd. The Oxisol and Ultisol soils, on the other hand, had higher Pb:Cd NERs because these soils demonstrated a marked preference for Pb, relative to Cd, at high affinity sites.

Sites of Pb and Cd Retention

Researchers have suggested that high affinity Pb and Cd sorption sites in soils and sediments may be different (Hansen and Maya, 1997; Pardo, 2000). However, our data indicated that Pb and Cd probably compete for many of the same high affinity sites. This was important in the Oxisol and especially in the Mollisol as Cd sorption at high affinity sites in these soils was lower when it was introduced to the soils after Pb compared to the

opposite sequence (Figs. 5-2 and 5-3). Also, Cd was more exchangeable when Pb and Cd were added to the soils at the same time in the Oxisol, Ultisol, and Mollisol soils with all (+100 %), 90 %, and 75 % of the latter metal being exchangeable, respectively (Fig. 5-4a). These data may be compared with values of 87, 87, and 23 % exchangeable Cd for the Oxisol, Ultisol, and Mollisol, respectively when it was added to the soils by itself (Figs. 5-2 and 5-3).

It is also interesting to note that the trend of Pb:Cd NERs of the soils from highest to lowest (Oxisol > Ultisol > Mollisol) followed the trend of proportions of variable charged surfaces in the soil samples (oxidic minerals, 1:1 phyllosilicates, and organic matter) and were opposite that of CEC. Therefore, on a relative basis, Pb compared to Cd had a very high specificity for variable charged surfaces compared to constant surface charge materials. It will be preferentially retained relative to Cd at these types of high affinity sorption sites regardless of when it enters the soil system (before, after, or with Ca and/or Cd). This was not surprising as much evidence has been presented supporting the conclusion that oxide mineral surfaces and organic matter have high affinities for heavy metals such as Pb and Cd (Bruemmer et al., 1983; Forbes et al., 1976; Jenne, 1968; McKenzie, 1980; Xia et al., 1997a, b) which were abundant in the Oxisol (Table 4-1).

In Figs. 5-2 and 5-3, it was apparent the amounts of exchangeable Pb and Cd changed little (exchangeable Pb or Cd in position E1 vs. E2 $p > 0.01$; exchangeable Cd in Mollisol excepted) in all soils regardless of when these metals were introduced to the soil systems. Therefore, the irreversible sorption of these metals evidently occurred at areas on the colloids different from the exchange sites. This was especially important for exchangeable Cd, after the soils had been previously exposed to Pb, as in most cases ≤ 50

% sorbed Pb was exchangeable. This left a large quantity of Pb sorbed to high affinity sites but did not change the quantity of exchangeable Cd.

Pb, Cd, and Ca Interactions

When metals are added together to soil systems, the interactions for sorption between ions can be either competitive, indifferent, or promotive (Davis and Kent, 1990). Competitive interactions between cationic adsorbates may occur through direct competition for surface sites or may be an indirect process whereby the adsorption of a cationic species results in changes in surface charge and/or surface protonation. Promotive interactions result when the promoter species changes the surface charge or surface protonation in such a way as to favor adsorption of the coadsorbing ion (indirect process; Wijnja and Schulthess, 2000).

Calcium and Cd had similar influence on Pb in the Oxisol and Ultisol. The amounts of sorbed and exchanged Pb in the presence of equal amounts of Cd (Fig. 5-4a) or Ca (Fig. 5-4b) were not significantly different ($p \geq 0.2$). Furthermore, relative to when Pb was introduced to these soils by itself (Fig. 5-2a and b), Cd and Ca decreased the amount of originally sorbed Pb by $\approx$ 10 % while having little effect on the non-exchangeable Pb fraction (Fig. 5-4a and b). Therefore, these metals had a minor competitive effect on Pb adsorption and did not compete with this metal for high affinity sorption sites. The similarities exhibited by Cd and Ca were not surprising in that Cd^{2+} and Ca^{2+} both have similar hydrated radii (4.26 and 4.12 Å, respectively; Nightingale, 1959) and filled valence orbitals (Cd^{2+} - $[Kr]d^{10}$; Ca^{2+} - [Ar]) which minimizes electron

sharing, thus, favoring coulombic type interactions with other charged species or surfaces (Huheey, 1983).

Echeverria et al. (1998) and Yong and Phadungchewit (1993) reported the competitive nature of various heavy metals in mineral and soil systems. They saw decreased sorption of Cd, Cu, Pb, and Zn when these metals were added together compared to when they were added in monometal form to soils. The former authors saw greater binding strength/retention of Pb as compared to Cd in soils. In a study looking at the extractability of sorbed Cu, Cd, Pb, and Zn with 1 *M* $MgCl_2$ on soil, Phillips (1999) witnessed nearly all sorbed Cd was exchangeable (> 90 %) while the exchangeable Pb fraction was only 35 % to 80 % of the originally sorbed amount. Also, Hansen and Maya (1997) observed ≥ 90 % of added Pb sorbed to suspended sediments in the presence of $CaCl_2$ (I = 0.05 *M*) while ≤ 70 % of the added Cd was sorbed under the same conditions.

This is contrary to Pb sorption by the Mollisol soil. The total amount of Pb sorbed by the Mollisol (Fig. 5-4a) in the presence of Cd was greatly and significantly ($p <$ 0.01) larger than when Pb was added by itself (Fig. 5-2c) or with Ca (Fig. 5-3c). However, the total amount of Pb + Cd sorbed to high affinity sites in this Sequence (5), was similar to the total amount of Pb + Cd sorbed in Sequences 1 and 3 (≈ 44 mmol kg^{-1}). Interestingly, this total amount of Pb + Cd sorbed in Sequences 1, 3, and 5 was less than the total amount Pb + Cd sorbed in Sequences 2 and 4 (≈ 54 mmol kg^{-1}). This reaffirms that Pb out-competes Cd for high affinity sorption sites in this soil. In Sequences 1, 3, and 5, Pb was added to the soils prior to Cd. In Sequences 2 and 4, Cd was introduced before Pb.

Also, this indicates that Pb and Cd compete for the same high affinity sorption sites in this soil. Salim et al. (1996) observed a similar event when extracting Cd, Ni, and Pb from clay-rich sediments spiked with > 1000 mg kg^{-1} metal using 1 *M* $MgCl_2$. Slight amounts of Pb were extracted while most of the Cd was found in the exchangeable fraction.

It was difficult to ascertain Ca's effect on Pb and Cd in the Ultisol and Mollisol as the amounts of sorbed Pb + Ca (Fig. 5-4b) or Cd + Ca (Fig. 5-4c) never exceeded their CEC values (11.01 and 20.92 $cmol_c$ kg^{-1}, respectively; Table 4-1; Phillips, 1999). However, in regards to the Ultisol, we noticed that most ($\geq$ 80 %) of the sorbed Cd and Ca were exchangeable (Figs. 5-4b and c) while only 39 % of the added Pb was exchangeable. In the Mollisol, > 100 % of the sorbed Ca was exchangeable indicating release of some residual Ca upon extraction with Na. However, 100 % of Pb was retained and $\approx$ 87 % Cd with the same extraction. Therefore, under the conditions of our experiment, Pb and Cd behaved similarly and were sorbed to high affinity sites (e.g. organic matter and 2:1 layer silicate interlayers) in this soil a priori while Ca acted as an exchanger.

In the Oxisol, Ca significantly reduced the amount of Cd sorbed as compared to monometal Cd addition (Figs. 5-4c vs. 5-2b, respectively). As with the other two soils, nearly all sorbed Ca was exchanged with Na and sorbed Cd + Ca represented $\approx$ 91 % of the Oxisol's CEC. Competitive sorption was observed between Cd and Ca as the number of sorption sites was limiting in this soil. The differences between soil colloid affinity for Pb as compared to Ca were also detected (Hansen and Maya, 1997).

Benjamin and Leckie (1981a, b) and Sarkar et al. (1999) have observed similar behavior in studies looking at the competitive adsorption of Cd, Pb, and Hg. They concluded that if two or more metals compete for the same binding sites, adsorption of a more strongly bound metal (e.g. Pb in our study) forces the more weakly sorbed metal to be retained at weaker sites (i.e. exchange sites).

Conclusions

Studies employing traditional approaches to sorption/desorption as well as sequential extraction techniques have provided valuable information regarding heavy metal interactions with soil surfaces as well as the partitioning of these species with various soil fractions. However, further important information was obtained in this study using a sequential sorption/desorption approach (Fig. 5-1). The sequential sorption procedure enabled determination of how Pb and Cd interact when introduced to soils at different times, the specificity soil sorption sites exhibit for one metal over another, as well as provided evidence for sorption mechanisms.

Due to Pb's chemical characteristics (relatively high electronegativity, low pK_H, small hydrated radius, electronic structure, etc.), this metal was sorbed in preference to Cd or Ca regardless of the order in which it entered soil systems. Cadmium, on the other hand, was sorbed and/or retained at high affinity sites to greater extent when added to the soils prior to Pb. Thus, at a contaminated site receiving Pb and Cd inputs at different times, Cd may be more mobile when introduced to soils after Pb compared to the opposite scenario.

Lead was much less exchangeable than Cd with ≤ 50 % and ≥ 80 % (Mollisol excepted; exchangeable fraction 0 - 38 %) originally sorbed metal being exchangeable, respectively. Furthermore, the ratios of non-exchangeable Pb:Cd indicated Pb inhibited Cd retention at high affinity sorption sites. This suggested that these metals compete for many of the same specific sorption sites. The Pb:Cd NERs followed the trend Oxisol > Ultisol > Mollisol demonstrating the preference and specificity Pb exhibits for variable charged surfaces which were abundant in the Oxisol. Also, following exchange, neither of the metals were capable of replacing the other from high affinity sorption sites to any large extent (≤ 0.7 mmol kg^{-1} metal).

The amounts of exchangeable Pb and Cd changed little regardless of when the metals were introduced to the soils. This suggests that the irreversible or Na-nonexchangeable sorption of these metals occurred at different sites from those of exchange. This was important for exchangeable Cd, after the soils had been previously exposed to Pb, as ≤ 50 % sorbed Pb was exchangeable in all sequences. This left a large quantity of Pb sorbed to high affinity sites while not changing the quantity of exchangeable Cd.

When metals were added together (e.g. Pb + Cd, Pb + Ca, or Cd + Ca), Pb again showed its ability to out-compete both Cd and Ca for exchange and high affinity sorption sites in our soils. Furthermore, Cd and Ca behaved similarly, especially in the Oxisol and Ultisol, predominantly functioning as exchangers in these soils. Both these metals competed slightly with Pb for exchange sites but had little influence on the non-exchangeable Pb fraction.

Due to Pb's high affinity for soil functional groups (especially oxidic surfaces), it is more likely to undergo inner-sphere surface complexation compared with either Cd or Ca. These reactions render this metal more stable, less labile, and decrease the threat of further soil contamination as compared to Cd.

Flow calorimetry, which directly measures the enthalpy change of a chemical reaction at the soil/water interface, coupled with adsorption isotherm data can be used to assess surface heterogeneity. Surface heterogeneity enables quantification of the differences in energy certain sorption sites may have for reactive species, such as Cd and Pb. This may allow us to determine which soil sorption sites (e.g. organic matter, Fe/Al oxides, etc.) are important and active in the retention of heavy metals.

CHAPTER 6
DETERMINATION OF THE SELECTIVITIES AND ENTHALPIES OF K/Ca AND K/Pb EXCHANGE AND SURFACE HETEROGENEITY IN TWO TROPICAL SOILS USING FLOW CALORIMETRY

Introduction

In many cases, much of the Pb in uncontaminated and contaminated soils is not present in readily available fractions (RAF; i.e. water-soluble and exchangeable with neutral salt). In several studies looking at the sequential extraction of Pb (and other heavy metals) from contaminated soils, researchers have shown the amount of Pb in the RAF relative to the total soil Pb is generally ≤ 1 % to 10 % (Boruvka et al., 1997; Kabala and Singh, 2001; Ma and Rao, 1997). This corresponded to RAF Pb ranging from ≈ 0.4 to 4,000 ppm (3.9×10^{-4} to 3.9 $cmol_c\ kg^{-1}$) using the high RAF value of 10 %. Thus, depending on a soil's CEC and the types of cations on the cation exchange sites, Pb potentially has the ability to occupy part or a majority of these sites.

The degree to which a cation adsorbs to an exchanger depends largely on its selectivity relative to other cations in the soil solution (McBride, 1994). A cation with high selectivity for a particular soil surface (exchanger) will be preferentially adsorbed relative to one with lower selectivity. Many studies, looking at the sorption of heavy metals (i.e. Pb, Cu, Zn, Cd, and Ni) added to soils and pure minerals (i.e. goethite, alumina, kaolinite, and zeolite), have inferred higher Pb selectivity relative to the other heavy metals based on differences in total amount of metals sorbed (Ahmed et al., 1998;

Gao et al., 1997; Gomes et al., 2001; Hong and Pintauro, 1996; Pardo, 2000; Shanableh and Kharabsheh, 1996; Yong and Phadungchewit, 1993). These studies have not focused on the exchangeable Pb fraction nor have they determined Pb selectivity relative to the important cationic nutrients commonly found on soil cation exchange sites (i.e. Ca, Mg, K, and Na). These cationic nutrients may compete strongly with Pb for adsorption.

Table 6-1 presents information on the amounts of exchangeable basic cations present on the exchange sites of three typical Puerto Rican soils. From the range of RAF Pb typically found in contaminated soils (3.9×10^{-4} to 3.9 $cmol_c\ kg^{-1}$), it is apparent that Pb can potentially compete strongly with certain cations for exchange sites based on concentration alone. Understanding how Pb competes for adsorption sites in soils, at varying concentrations and saturations on the exchanger relative to a typical cation (i.e. Ca or K), would provide useful information about Pb selectivity and, thus, mobility and diffusion in soils.

Table 6-1: Neutral 1 *M* $NH_4C_2H_3O_2$ exchangeable basic cations of three Puerto Rican soils.

	Ca^{2+}	Mg^{2+}	K^+	Na^+
Soils	$cmol_c\ kg^{-1}$			
Mollisol	16.3	3.1	0.9	0.6
Oxisol	0.6	0.8	0.1	0.1
Ultisol	2.9	0.5	0.5	0.6

Flow calorimetry (FC), which directly and quantitatively measures the heat of a reaction on soil surfaces (Rhue et al., 2002), coupled with information about ion selectivity (i.e. data from exchange isotherm experiments) provides a means to ascertain reactions occurring at the soil/water interface. This leads to an understanding of the

binding strength of a particular reactive species to soil surfaces. Also, this provides information about surface heterogeneity or knowledge of how this binding strength varies with different amounts of a particular cation on an exchanger . Thus, different types of exchange/sorption sites can be identified within a heterogeneous structure like soil (Goulding, 1983).

No known research has determined the surface heterogeneity of soils using FC nor has anyone studied K/Pb and K/Ca systems using this technique. Therefore, the objectives of this research were i) to study and compare exchange reactions involving K^+/Ca^{2+} and K^+/Pb^{2+} using calculated selectivity coefficients in two highly weathered tropical soils. Lead and Ca were chosen as Pb is an important cationic contaminant in soils worldwide (Brown et al., 1999; Nriagu, 1998) and is known to undergo both chemisorption and physisorption reactions with soil surfaces. Calcium, on the other hand, is generally regarded as a physisorbing cation commonly found in high relative concentrations on soil cation exchange sites (McBride, 1994; Sparks, 1995). The other objectives of this study were ii) to determine enthalpies of sorption of K/Ca and K/Pb systems using FC, and iii) to ascertain the surface heterogeneity of these cation systems in these soils.

Materials and Methods

Soil Samples

The surface horizons (0 - 15 cm) of the Puerto Rican Oxisol and Ultisol were sieved to an aggregate size of between 0.25 and 0.5 mm prior to being used in this study. These tropical soils were selected for study because relative to their temperate region

counterparts, little is known about the thermodynamics and selectivity of K/Ca and K/Pb exchange in these systems. The important mineralogical and chemical properties of these soils were obtained using standard methods and are presented in Table 4-1 (pg. 50).

Determination of Exchangeable Cations

Duplicate columns, for each soil type, holding between 3 to 5 g of soil were constructed (and weighed) to allow for unsaturated flow (Fig. 6-1). Solutions containing differing amounts of KNO_3 and/or $Ca(NO_3)_2$ or KNO_3 and/or $Pb(NO_3)_2$ were passed through the soil using a combination of gravity and a suction of 20 cm of water applied to the bottom of the column. The solution compositions were as follows: 15 m*M* KNO_3, 14.25 m*M* KNO_3 + 0.25 m*M* $M(NO_3)_2$, 13.5 m*M* KNO_3 + 0.5 m*M* $M(NO_3)_2$, 12 m*M* KNO_3 + 1 m*M* $M(NO_3)_2$, 9 m*M* KNO_3 + 2 m*M* $M(NO_3)_2$, 6 m*M* KNO_3 + 3 m*M* $M(NO_3)_2$, 3 m*M* KNO_3 + 4 m*M* $M(NO_3)_2$, and 5 m*M* $M(NO_3)_2$ where $M^{2+} = Ca^{2+}$ or Pb^{2+}. The ionic strength (*I*) and pH of each solution were 15 m*M* and 4.7, respectively. The pH of the solutions was adjusted with 10 m*M* HNO_3. The adjustment of solution pH resulted in changes of $I \leq 0.2$ %. It was necessary that both the pH and *I* of each of the solutions were matched. Changes in soil solution pH and *I* lead to changes in the surface charge of variably charged soil colloids, thus, metal adsorption in these systems changes (Uehara and Gillman, 1981; van Olphen, 1977).

Soil columns were flushed with 20 mL ($\approx$ 20 pore volumes assuming 5 g soil and a gravimetric water content of 0.2) of 0.5 *M* KNO_3. All flushes were in 10 mL aliquots unless stated otherwise. This was followed by passing 40 mL of 15 m*M* KNO_3 through the columns in order to ensure soils were K-saturated prior to the start of any adsorption

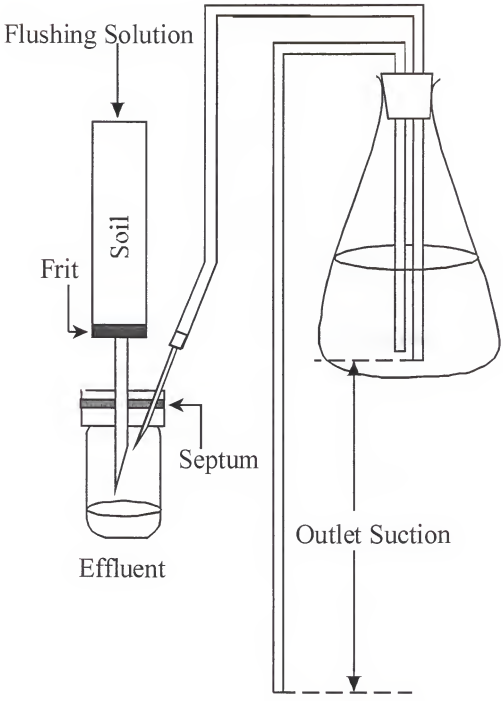

Figure 6-1. Typical unsaturated flow column set-up used in adsorption experiments.

experiments. The latter flushing solution was used to ensure soil solutions had an $I = 15$ mM. The K/Ca and K/Pb solutions were then added to the soils until the concentrations

in the column effluents were C/C_o (effluent/eluent) = 1 and 0.95 for K/Ca and K/Pb, respectively (usually ≥ 100 pore volumes).

After solution equilibration, the columns + wet soils were weighed in order to correct for any occluded K, Ca, and/or Pb remaining in the soil pores. The adsorbed metals were then extracted with 5 washes of 5 mL aliquots of 0.5 *M* $Mg(ClO_4)_2$. The effluent was collected and refrigerated for later analysis of K^+, Ca^{2+}, and Pb^{2+} on the flame atomic absorption spectrophotometer (AAS). Preliminary experiments indicated this amount of $Mg(ClO_4)_2$ satisfactorily desorbed all exchangeable K, Ca, and Pb. Duplicate values of metal concentration at each concentration step were averaged and standard deviations calculated.

Each of the soils to which different concentrations of Pb were added were removed from the columns, dried, and digested in concentrated HNO_3 according to U.S. EPA Method 3051 (U.S. EPA, 1996). This was done to ascertain levels of non-exchangeable Pb in the samples. Furthermore, subsamples (≈ 2 at each Pb step) of these soils were looked at under a scanning electron microscope coupled with energy dispersive x-ray spectroscopy (SEM-EDX). This was done to determine discrete Pb phases/associations within the soils. The soils undergoing Ca additions were re-equilibrated with KNO_3 and the cycle of solution addition, as described above, was repeated.

Determination of Equilibrium Selectivity Coefficients

Heterovalent exchange reactions ($A^{2+} \rightarrow B^+$) in the tropical soils were studied according to the generic reaction,

$$A^{2+} + 2BX \leftrightarrow AX_2 + 2B^+ \qquad [6\text{-}1]$$

$$K_{EX} = \left(a_{AX_2} \bullet a_B^2\right) / \left(a_{BX}^2 \bullet a_A\right) \qquad [6\text{-}2]$$

where X represents 1 mole of negative charge per unit mass of soil, A^{2+} is either Ca^{2+} or Pb^{2+}, B^+ equals the amount of monovalent cations ($K^+ + H^+$) reacting in the system, K_{EX} is the equilibrium constant for the exchange reaction, and (a) represents the activity of the cations. Hydrogen was grouped with K^+ as our data and other research have shown that the exchange selectivity for the proton on pure clays, resins, and soils is near that for K^+ and Na^+ (Coulter, 1969; Foscolos and Barshad, 1969; Rhue and Mansell, 1988).

The Gaines-Thomas approach, which assumes the activity of adsorbed cations equals their equivalent fractions on the exchanger (E; $mmol_c\ kg^{-1}$), was used to calculate selectivity coefficients (K_{GT}).

$$K_{GT} = \left(E_{AX_2} \bullet a_B^2\right) / \left(E_{BX}^2 \bullet a_A\right) \qquad [6\text{-}3]$$

Activities (a) in Eq. [6-3] were calculated as products of single-ion activity coefficients, as estimated with the extended Debye-Hückel equation , and single-ion molar concentrations in the equilibrium solutions (McBride, 1994).

A thermodynamic nonpreference isotherm for heterovalent cation exchange (Eq. 6-1) was calculated with the equation (Sposito et al., 1983)

$$E_j = 1 - \left[1 + \frac{2}{rTN}\left(\frac{1}{E_i^2} - \frac{1}{E_i}\right)\right]^{-1/2} \qquad [6\text{-}4]$$

where E_j is the equivalent fraction of adsorbed divalent cation (Ca^{2+} or Pb^{2+}), E_i is the equivalent fraction of monovalent cation in the equilibrium solution, r is γ_B^2/γ_A where γ_A and γ_B are single-ion activity coefficients of cations A^{2+} and B^+, and TN is equal to the total cation concentration in $mol_C\ L^{-1}$.

The thermodynamic nonpreference isotherm is delimited by having (i) the standard Gibbs free energy of the exchange reaction (ΔG_{EX}°) equal zero (i.e. system at equilibrium) and (ii) the exchanger phase activity coefficients are unity (ideal mixture). Therefore, according to chemical thermodynamics, cation exchange does not exhibit selectivity if $K_{EX} = 1$ and the exchanger phase exhibits properties of an ideal solid solution (Sposito et al., 1983).

Calorimetric Measurements

Heats of exchange (ΔH) were directly determined using a flow calorimeter (Rhue et al., 2002). Amounts of 50 to 100 mg of soil were placed in the column of the FC and saturated with 15 m*M* KNO_3. The 5 m*M* $Ca(NO_3)_2$ solution was then reacted with the K-saturated soils and heats of exchange were ascertained. The K and Ca solutions were cycled through the soils several times. This was done to check for heterogeneity between soil samples and, thus, enabled determination of a correction factor. This factor corrected for differences in soil samples, within a soil order, based on exchange thermodynamics and not soil weight. This ensured the systems were behaving normally when the K and Ca peak areas were of equal and opposite magnitude which is indicative of an exchangeable/reversible process.

Once the K/Ca cycles were complete, one of the solutions from the exchange experiment (excepting 14.25 m*M* KNO_3 + 0.25 m*M* $Pb(NO_3)_2$ for the Oxisol as the heat of exchange of Pb was below the detection limit of the FC) was reacted with a K-saturated soil and the heat was determined. The 15 m*M* KNO_3 solution was then reacted with the $M(NO_3)_2$ or KNO_3 + $M(NO_3)_2$ equilibrated soil and the heat ascertained to

determine if the exchange reactions were reversible. This process was repeated 3 to 6 times for each solution composition. The heat data were averaged and standard deviations calculated.

Each of the soils reacted with different concentrations of Pb then underwent cycles of 15 m*M* KNO_3/5 m*M* $Ca(NO_3)_2$. This was done to enable a comparison between the original (i.e. prior to Pb introduction to the soils) energetics of K/Ca exchange and the post-Pb energetics of K/Ca exchange. This enabled determination of changes in the energetics of cation exchange as a function of Pb introduction. These soil samples were then removed from the FC columns, dried, and digested in concentrated HNO_3 (U.S. EPA, 1996) as before. The digestates were refrigerated until the Pb was analyzed on the flame AAS. The soils were digested to ascertain levels of non-exchangeable Pb^{2+} in these soil samples. The soils receiving Ca additions were re-equilibrated with 15 m*M* KNO_3, as described above, followed by reaction with one of the different equilibrating solutions.

Determination of Surface Heterogeneity

Surface heterogeneity was determined by plotting the column adsorption data vs. the calorimeter data at each concentration step . Lines/curves were then fit to the data points and equations derived to give an indication of the integral heat of adsorption. The derivative of these equations, when plotted vs. the column adsorption data, yielded the differential plots or an indication of surface heterogeneity. Surface heterogeneity allows for changes in heats of adsorption, of a reactive species, with changes in surface composition to be ascertained.

Results and Discussion

CEC Differences Under Ca^{2+}, Pb^{2+}, and K^+ Saturation

The CECs of the soils were different in the 3 cationic systems (Ca^{2+}, Pb^{2+}, and K^+) in this study. This was determined by extraction of these cations from soils saturated with 5 m*M* $Ca(NO_3)_2$, 5 m*M* $Pb(NO_3)_2$, or 15 m*M* KNO_3, respectively (Table 6-2). The Ca^{2+}-saturated soils yielded the highest CECs followed by those that were Pb^{2+}-saturated. The K^+-saturated soils gave the lowest values of CEC. Deist and Talibudeen (1967), Maes and Cremers (1977), and Rhue and Mansell (1988) have all shown higher measured CECs with divalent cations compared to monovalent ones. The differences in CEC between the two types of systems were due, at least in part, to the inclusion of H^+ in the ion exchange process.

Table 6-2. CEC† of the Oxisol and Ultisol as a function of the saturating cation.‡

	Ca^{2+}	H_{Ca}^+	K^+	H_{Pb}^+	Pb^{2+}
Soil			$mmol_c\ kg^{-1}$		
Oxisol	60.0(±2.3)	31.9(±4.6)	28.1(±4.0)	14.4(±4.1)	42.5(±0.7)
Ultisol	129.6(±6.6)	31.7(±9.0)	97.9(±6.1)	14.4(±6.6)	112.3(±2.4)

†Numbers in parenthesis are standard deviations of the means.
‡CEC of $K + H_{Ca}^+$ = CEC in Ca^{2+}; CEC of $K^+ + H_{Pb}^+$ = CEC in Pb^{2+} where H_{Ca}^+ and H_{Pb}^+ are the amounts of exchangeable H^+ found by subtracting CEC in K^+ from the CEC in Ca^{2+} and Pb^{2+}, respectively.

At pH 4.7, the equilibrium pH of all solutions used in this study, previous research on the Oxisol and Ultisol indicated that Al^{3+} and Fe^{3+} were not solubilized from the soils and, thus, did not participate in cation exchange. Our soils possessed significant

amounts of colloidal Fe/Al oxides and organic matter (≈ 48 and 19 % for the Oxisol and Ultisol, respectively) which have high affinities for H^+ (Barrow, 1987; van Olphen, 1977). This strongly suggests that H^+, in the presence of K^+ on the exchanger in our systems, made up the difference in CECs in the monovalent vs. divalent systems.

It is interesting to point out the differences in CEC measured in the divalent cation systems, Ca^{2+} vs. Pb^{2+}, by our soils. The Oxisol and Ultisol had (17.5 and 17.3 $mmol_c$ kg^{-1}, respectively) more CEC when Ca^{2+}-saturated as compared to Pb^{2+}-saturated conditions (Table 6-2). Speciation calculations performed by Visual Minteq (Gustafsson, 2000) showed that, in the Pb solution, the main species were Pb^{2+} and $PbNO_3^+$ (≈ 92 and 8 % of the total Pb in solution, respectively). The main species in the Ca solution was Ca^{2+} (> 98 %) while $Ca(NO_3)^+$ was < 2 % of the total Ca in solution. The relatively high amount of monovalent $PbNO_3^+$ in the Pb solution decreased the CEC relative to the CEC measured in Ca. This was due to the increased ability of H^+ to compete for cation exchange sites with $PbNO_3^+$.

Determination of Ca and Pb Selectivity

The preference of a given ion for an exchanger is given by the selectivity coefficient (Helfferich, 1962). Values of the experimentally determined selectivity coefficients (K_{GT}) for $Ca^{2+} \rightarrow K^+ + H^+$ and $Pb^{2+} \rightarrow K^+ + H^+$ exchange reactions on the Oxisol and Ultisol soils are displayed in Fig. 6-2. All compositions of $K^+ + H^+$, Ca^{2+}, or Pb^{2+} on the exchanger yielded Ca^{2+} and Pb^{2+} selectivity coefficients < 1 for the two soils studied. This meant that $K^+ + H^+$ had a greater selectivity for soil cation exchange sites. Plotting equivalent fractions of adsorbed divalent cations vs. their equivalent fractions in solution

along with the nonpreference isotherm (Eq. 6-4), highlights this point (Fig. 6-3). It is evident from this figure, that all soil-metal curves were below the nonpreference isotherm. This provides further evidence for the higher relative K^++H^+ selectivity in the Oxisol and Ultisol.

Many investigators have shown higher selectivity for K^+ over Ca^{2+} in kaolinite and kaolinitic soils, which was an abundant mineralogical component of our soils (Oxisol and Ultisol are 49 and 45 % kaolinite in their clay fractions, respectively), at most K/Ca ratios on the exchanger (Levy et al., 1988; Levy and Hillel, 1968; Udo, 1978; van Bladel and Gheyi, 1980). This is at least partly due to the fact that most clays behave as weak field exchangers. This means that the charge density of soil clays is generally not great enough to remove water of hydration from adsorbing cations. Therefore, selectivity may be related to the hydrated charge density and hydration energy (ΔH_{hyd}; kJ mol^{-1}) of a particular adsorbing cation (Juo and Barber, 1969; Rhue et al., 2002).

The order of increasing charge density (mol_c m^{-2}) for several important colloidal materials commonly found in soils is goethite (pH = 9; 4.27 x 10^{-7}) < smectite (1.27 x 10^{-6}) < vermiculite (3.13 x 10^{-6}) < kaolinite (6.40 x 10^{-6}) < organic matter (7.74 x 10^{-6}) (McBride, 1994; Thompson et al., 1989). The order of increasing hydrated charge density (cation valence/hydrated radius, Å) and ΔH_{hyd} (kJ mol^{-1}) of the important cations in our study is K^+ (0.30) < Ca^{2+} (0.49) < Pb^{2+} (0.50) and K^+ (-321) < Pb^{2+} (-1480) < Ca^{2+} (-1592), respectively (Nightingale, 1959; Wulfsberg, 2000). Due to kaolinite's relatively high charge density, allowing it to dehydrate or partially dehydrate weakly hydrated cations (i.e. K^+), as well as its abundance in the chemically active fraction of our soils, it was not surprising the Oxisol and Ultisol had a preference for K^+ over Ca^{2+} or Pb^{2+} at all

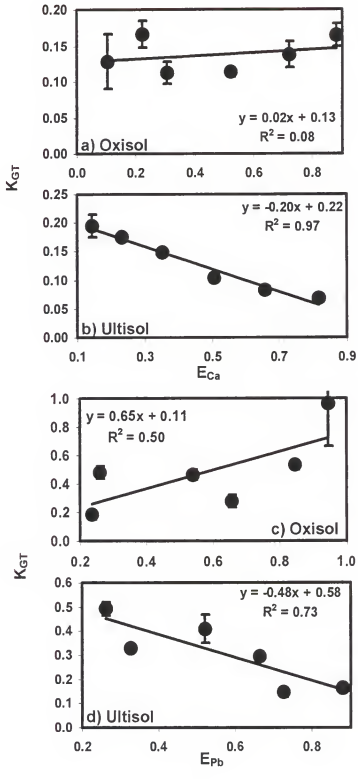

Figure 6-2. Gaines-Thomas selectivity coefficients (K_{GT}) vs. equivalent factions of Ca^{2+} on the exchanger in a) Oxisol and b) Ultisol or Pb^{2+} on the exchanger in c) Oxisol and d) Ultisol.

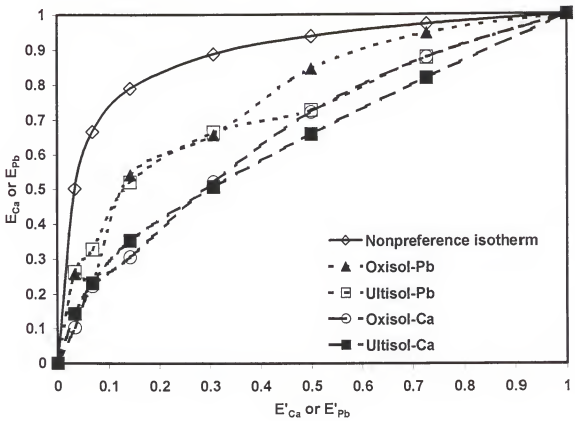

Figure 6-3. Exchange isotherms for Pb^{2+} and Ca^{2+} replacing K^+ on exchange sites as well as heterovalent exchange nonpreference isotherm on the Oxisol and Ultisol soils. E_{Ca} and E_{Pb} = equivalent fractions of either Ca^{2+} or Pb^{2+} on the exchanger and E'_{Ca} and E'_{Pb} = equivalent fractions of either Ca^{2+} or Pb^{2+} in the equilibrium solution.

ratios of K^+ in our study.

Generally, the selectivity of a preferred ion on the exchanger increases with decreasing saturation of that ion (Gast, 1972). In Fig. 6-2, it is evident that this holds true for the Ultisol soil but not for the Oxisol. The negative slopes of the Ultisol-Ca and -Pb lines (Figs. 6-2b, d) indicate that as the amount of K^+ on the exchanger decreases, its selectivity increases (going from left to right on the figs.). Contrarily, the Oxisol-Ca and -Pb lines remain relatively constant or slightly increase with increasing divalent metal saturation (i.e. K_{GT} stays the same/decreases with decreasing K^+ saturation).

The data suggests that, in the Ultisol, there were exchange sites possessing different binding energies for K^+ (Gast, 1972). At low amounts of K^+ on the exchanger, this cation was predominantly retained by higher energy sites. With increasing K^+ saturation on the exchanger, these higher energy sites became saturated and K^+ then went to sites possessing lower affinity for this ion. The Ultisol soil had ≈ 17 % interstratified smectite in the clay fraction. This mineral tends to hold onto K^+ tightly in its interlayer and most likely comprised the high energy K^+ binding sites. In a thermodynamic study looking at Ca/K exchange in 2 soils, Sparks and Jardine (1981) found that the binding energy of K^+ was larger in the soil having more interlayer surface charge compared to the one having less 2:1 phyllosilicate minerals.

The Oxisol-Ca and -Pb lines do not display a definite increase or decrease in selectivity which was indicated by the low R^2 values. The selectivities for these metals may be considered unchanging with changes in cation composition on the exchanger. This soil did not possess any interlayer exchange sites as did the Ultisol. It was composed of minerals having only external exchange sites (Table 4-1, pg. 50). Therefore, the data suggest that these external binding sites all exhibit similar affinity and binding energy for K^+ (Gast, 1972).

Enthalpies of Ca/K and Pb/K Exchange (ΔH_{EX}) Using Flow Calorimetry

Flow calorimetry enables the direct measurement of the heat associated with a reaction (Rhue et al., 2002; Steinberg, 1981). This is related to the enthalpy change (ΔH) which, in the case of ion surface reactions on soils, provides information about the binding strength of a particular ionic species to/on a soil surface (Goulding, 1983; Sparks

and Jardine, 1981). The ΔH corresponds to the experimental conditions used and not the standard state. However, to convert the experimental enthalpy (ΔH) to the standard state enthalpy ($\Delta H°$; as determined by the temperature dependence of the sorption isotherm) requires correcting for the enthalpy of dilution of the salts used, from the final state to infinite dilution (Goulding, 1983). The differences between ΔH and $\Delta H°$ have been shown to be small and are generally $\pm$ 5 to 9 % (Barrer et al., 1963; Goulding, 1983; Laudelot et al., 1968). Furthermore, preliminary experiments showed the flow calorimeter, by design, corrects for ΔHs associated with the solvation of the soil, dilution of salt solutions when mixed, and mixing processes within the instrument. Thus, comparisons between the experimentally determined ΔH by the FC and $\Delta H°$ are justified.

Table 6-3 presents the ΔHs associated with the exchange reactions of Ca→K and Pb→K in the Oxisol and Ultisol. The adsorption of Ca^{2+} and Pb^{2+} was endothermic when replacing K^+ which is consistent with most of the literature for both metals (Deist and Talibudeen, 1967; Elkhatib et al., 1993; Laudelot et al., 1968; Maes and Cremers, 1977; Parida et al., 1996; Rodda et al., 1996; Scheinost et al., 2001; Udo, 1978). Furthermore, the ΔH of Pb adsorption was significantly less ($p \leq 0.1$; Oxisol Pb→K vs. Ultisol Ca→K excepted) than that of Ca^{2+} for both soils. This means that the binding energy for Ca^{2+} was stronger than that for Pb^{2+} and that it took more energy for Ca^{2+} rather than Pb^{2+} to replace K^+ from soil. This was most likely due to the fact that Pb^{2+} has a lower ΔH_{hyd} and a slightly higher hydrated charge density than Ca^{2+} facilitating replacement of K^+ relative to Ca^{2+}.

Table 6-3. Heats of exchange[†] (ΔH; kJ mol_c^{-1}) for the Oxisol and Ultisol.

Soil	Ca→K	Pb→K
Oxisol	7.53(±1.36)a[‡]	5.61(±0.51)a
Ultisol	10.63(±1.17)b	7.72(±0.28)c

[†]Numbers in parenthesis are standard deviations of the means.
[‡]Means within a column or row with the same letter are not significantly different at $p \leq 0.1$.

The ΔH values were significantly larger ($p \leq 0.1$) for the Ultisol than the Oxisol. This indicated that it took more energy for Ca^{2+} and Pb^{2+} to replace K^+ in the Ultisol. As explained earlier, this was due to presence of 2:1 layer silicates in the Ultisol and not in the Oxisol. The interlayer space in these minerals has been shown to have a high selectivity for K^+ making its replacement by divalent cations difficult (Gast et al., 1969; Sparks and Jardine, 1981).

In previous work, the $\Delta H°$ for Ca→K exchange on a variety of soils ranged from 3.3 to 16.3 kJ mol_c^{-1} (Deist and Talibudeen, 1967; Goulding and Talibudeen, 1984; Ogwada and Sparks, 1986; Sparks and Jardine, 1981), consistent with our values as measured by flow calorimetry. Most of these soils were dominated by 2:1 layer silicates whereas the two soils used in this study were dominated by kaolinite and metal oxides. Reports of ΔH or $\Delta H°$ for exchange on highly weathered soils dominated by kaolinite and oxides are few. However, Udo (1978) reported a $\Delta H°$ of 54.5 kJ mol_c^{-1} for K/Ca exchange on a kaolinitic soil clay. Our Oxisol and Ultisol samples contained 56 and 59% clay, respectively, of which about half was kaolinite. Thus, on a per gram of clay basis, the ΔH for K/Ca exchange on the Oxisol and Ultisol was 13.4 and 18.0 kJ mol_c^{-1}, respectively. Attributing all of the heat to just the kaolinite fraction would increase these

numbers to only about 27 and 36 kJ mol_C^{-1}, considerably below the value reported by Udo (1978).

Kaolinite clay exhibits higher selectivity toward K relative to Ca compared with 2:1 layer clay minerals. This has been attributed to the higher surface charge density of kaolinite (Deist and Talibudeen, 1967; Levy and Hillel, 1968; Levy et al., 1988; Udo, 1978; van Bladel and Gheyi, 1980). Since a higher selectivity toward K could result from a higher binding strength and thus a higher ΔH of exchange, the discrepancy between Udo's value and ours could have resulted from differences in surface charge density. However, this was not the case. His Ca-saturated clay fraction had a CEC = 18.1 $cmol_C\ kg^{-1}$ while the CECs of our Ca-saturated Oxisol and Ultisol were 6.0 and 13.0 $cmol_C\ kg^{-1}$, respectively (Table 6-2). If the CEC in our soils is put on a per gram of clay basis, the CEC would be 11 and 22 $cmol_C\ kg^{-1}$, consistent with Udo's value for CEC of the clay fraction he studied.

The thermodynamics of Pb exchange and sorption reactions on soils and mineral specimen clay have been studied much less extensively than those reactions involving Ca. In a Brazilian soil high in kaolinite and gibbsite, Airoldi and Critter (1997) found $\Delta H°$ for Pb adsorption was -43.0 kJ mol_C^{-1} using the temperature dependence of the Langmuir isotherm. The researchers only considered adsorption of Pb^{2+} on the soil surface and did not specify which cation/s Pb^{2+} was replacing. Thus, it is difficult to draw any conclusions from this work. Lopez et al. (1995) and Lopez-Delgado et al. (1998) suggested Pb^{2+} adsorption on blast furnace sludge, which is 47 and 34 % Fe_2O_3 and carbon, respectively, occurred via the replacement of Ca^{2+} (i.e. cation exchange) and

found $\Delta H°$ was endothermic (26.1 ± 3.1 kJ mol_c^{-1}). However, they did not make an effort to partition the enthalpy change between physi- and chemisorption of Pb.

At constant pH = 5.5, Rodda et al. (1996) determined ΔH for sorption of Pb on goethite was 8.2 ± 5.5 kJ mol_c^{-1} using the temperature dependence (10° to 70° C) of several sorption models (Langmuir two-site, FDM surface precipitation, and BET models). At this pH and 25° C, the goethite surface was positively charged (point of zero charge = 8.3) which would suggest chemisorption of Pb to the goethite surface was the likely mechanism of metal retention. However, increasing temperature lowers the point of zero charge due to a decrease in pK_w (-log of the ionization constant of H_2O). Also, formation of Pb hydrolysis species [$Pb(OH)^+$, $Pb(OH)_2^0$, $Pb(OH)_3^-$, etc.] increases with increasing temperature (Rodda et al., 1993). At pH 6 to 8 and 25° C, Bargar et al. (1997a, b) have suggested the dominant Pb species which sorbs to Fe/Al oxide surfaces exists as $Pb(OH)_3^-$. These observations suggest Pb could have been both chemi- and physisorbed to goethite surfaces. Therefore, it is not possible to associate the ΔH of Pb sorption on Rodda et al.'s goethite to a particular mechanism. Our values for $Pb \rightarrow K$ exchange of 5.61 and 7.72 kJ mol_c^{-1} for the Oxisol and Ultisol, respectively were closest to those determined by Rodda et al. (1996). However, these ΔH values corresponded to Pb physisorption as will be explained below.

Flow calorimetry allows multiple sorption/desorption cycles to be applied to the same sample. This enables the thermodynamics of reversible and irreversible reactions to be determined (Rhue et al., 2002). In all soil samples subjected to Pb^{2+} solutions in our experiment, there were no significant differences in the heats of Pb sorption or desorption, there were no significant discrepancies in the heats associated with repetitive

Pb sorption/desorption cycles (on the same sample), and ΔHs associated with K/Ca exchange before and after the introduction of Pb to our soils were not significantly different. Furthermore, from Table 6-4, it is apparent that Pb was irreversibly sorbed by both the Oxisol and Ultisol soils.

Table 6-4. Nonexchangeable Pb† in column adsorption vs. calorimeter studies.

	Adsorption study	Calorimeter study
Soil	mg kg^{-1}	
Oxisol	2975(±694)a‡	3469(±1754)a
Ultisol	1848(±472)b	1891(±764)b

†Numbers in parenthesis are standard deviations of the means.
‡Means within a column or row with the same letter are not significantly different at $p \leq 0.05$.

Two conclusions can be drawn from these findings. First, Pb chemisorption on our soils was either not energetic enough for detection by the flow calorimeter or it was completely driven by a change in entropy (ΔS). This was because the only reaction involving an enthalpy change was associated with ion exchange of Pb^{2+} on soil surfaces. Second, Pb chemisorption occurs on different sites than cation exchange reactions. Lead chemisorption did not change the energetics of K/Ca exchange nor did it change the CEC of our soils.

The data suggest Pb chemisorption was driven by ΔS as the detection limit of the instrument is low ($\Delta T \approx 8 \times 10^{-4}$ °C or ≈ 0.3 mJ; Rhue et al., 2002) relative to the magnitude of the enthalpies we determined for Pb^{2+} adsorption (Table 6-3). The loss of Pb^{2+} from the solution phase and its replacement, in the solution phase, by H^+, OH^-, and/or H_2O would result in a positive ΔS in the solution phase. The solution would be

less ordered by K^+ relative to Pb^{2+}. Similar observations have been made by others looking at heterovalent exchange in soils (Gast et al., 1969; Laudelot et al., 1968; Maes and Cremers, 1977; Sparks and Jardine, 1981).

In spite of this information, it is difficult to imagine the chemisorption of Pb not having any heat effect. This reaction involves the breaking of bonds followed by the subsequent formation of covalent bonds between Pb and soil surface functional groups (Bargar et al., 1997a, b, 1998; Xia et al., 1997a, b). Therefore, Pb chemisorption is probably mostly driven by an entropy change and slightly propelled by an enthalpy change so low it is undetectable by the FC.

Nonexchangeable Pb

Lead has been shown to readily undergo chemisorption reactions in a variety of soils, organic matter, and pure minerals (Bargar et al., 1998; Davis and Leckie, 1978; Eick et al., 1999; Pardo, 2000; Phillips, 1999; Strawn et al., 1998; Strawn and Sparks, 1999; Xia et al., 1997b; Zhang et al., 1997). The ability of Pb to take part in this type of reaction has been attributed to the relatively high affinity of Pb for most functional groups in organic matter, which are hard Lewis bases - carboxylic and phenolic groups (Pb^{2+} is a borderline hard Lewis acid); Pb's electronegativity (2.10), enabling it to pull electron density away from soil surface functional groups during bond formation; and its relatively low pK_H (negative log of hydrolysis constant, 7.78) allowing it to form chemical bonds with soil surfaces in hydrolyzed form (Bruemmer et al., 1986; Forbes et al., 1976; Huheey, 1983; McBride, 1994).

The Oxisol soil irreversibly sorbed ≈ 3000 to 3500 ppm Pb while that value for the Ultisol was ≈ 1900 ppm (Table 6-4). The Oxisol had a greater abundance of both organic matter (4.1 and 1.9 % for the Oxisol and Ultisol, respectively) and iron/aluminum oxides (28.7 and 8.6 % for the Oxisol and Ultisol, respectively) compared to the Ultisol (Table 4-1; pg. 50). These components probably accounted for the greater chemisorption of Pb in the Oxisol as both materials have been shown to be important in the irreversible sorption of heavy metals and especially Pb (Bargar et al., 1997a, b; Gao et al., 1997; Gong and Donahoe, 1997b; Jenne, 1968; Kinneburgh et al., 1976; Sauve et al., 2000; Sauve et al., 1998b).

The SEM-EDX was used to identify specific phases of Pb on the soil surfaces. Both soils showed discrete Pb-C phases (Fig. 6-4). The C was from organic matter as $PbCO_3$ was not stable under experimental conditions. The elemental dot maps show where Pb-C are present together. In these areas, the other elements (i.e. Al, Fe, O, and Si) are absent. It seems unlikely O was not part of the Pb-C phase as Xia et al. (1997a, b) have shown the C-O functional groups are important in Pb chemisorption to organic matter. However, if Pb was associated with sulfhydral groups from organic matter, it would be possible O was not present in this area. It is difficult to unequivocally determine if Pb was associated with S in our soils as the absorption edges for these elements overlap (Pb, $M\alpha$ = 2.346 keV and S, $K\alpha$ = 2.308 keV). Elucidation of the importance of S in Pb chemisorption requires further research.

The instrument Pb detection limit was ≈ 3,000 ppm (Wayne Acree; personal communication), thus, it is possible not all discrete Pb phases were detected. However, solid phase precipitation was ruled out as a retention mechanism under the conditions of

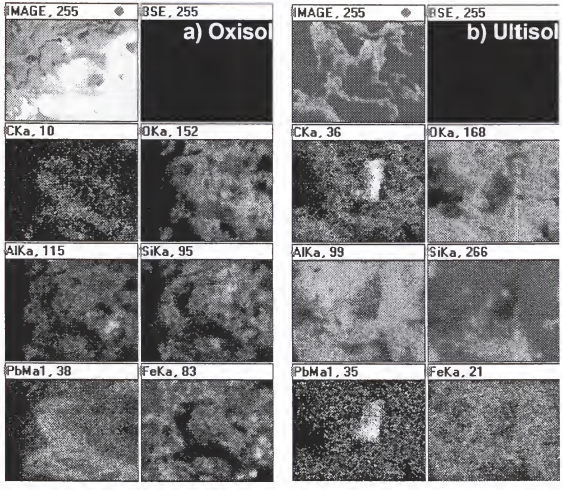

Figure 6-4. SEM-EDX elemental dot maps of a) Oxisol and b) Ultisol soil samples. Light areas of the dot maps indicate elevated concentrations of a particular element.

our study due to the low reaction pH 4.7 and relatively low Pb concentrations. Visual Minteq (Gustafsson, 2000) confirmed soil solutions were undersaturated with respect to $Pb(OH)_2$ and $PbCO_3$ ($P_{CO_2} = 10^{-3.5}$ atm). Thus, inner-sphere complexation reactions were the most likely nonexchangeable retention mechanisms involving Pb and Oxisol and Ultisol surfaces.

Surface Heterogeneity

Many models have been proposed aimed at describing the sorption of a reactive species on soil surfaces. Arguably, the most commonly employed model describing metal sorption is the Langmuir isotherm. An important shortcoming of this model is that it assumes all sites on the sorbing medium are the same. However, due to the heterogeneous nature of soil and even single component pure mineral specimens (i.e. goethite having three different types of OH groups and smectite having interlayer, edge, and external adsorption sites), it is known that there often exist several different types of sorption sites. The use of the ΔH of adsorption for a series of ratios of Ca:K or Pb:K coupled with adsorption isotherm data for the same cationic ratios enabled the determination of the integral ΔH of adsorption of Ca or Pb (Figs. 6-5a, b and 6-6a, b). An equation was then derived, when a straight line or smooth curve was fit through the data points. Taking the derivative of the equation and re-plotting the data yields the differential ΔH of exchange. This provides an indication of surface heterogeneity (Figs. 6-5c, d and 6-6c, d; Goulding, 1983).

Figs. 6-5 and 6-6 indicate that adsorption of Ca^{2+} and Pb^{2+} was more dependent on soil composition than metal type. Straight lines ($R^2 \geq 0.94$) were fit through the Ca and Pb data points in the Oxisol while a quadratic fit ($R^2 \geq 0.95$) of the data points was most appropriate for the same metals in the Ultisol.

The derivative of the equations of the straight lines indicated that as the exchange sites in the Oxisol became increasingly Ca^{2+} or Pb^{2+} saturated, the heat that it took to replace the remaining K^+ ion did not change (Figs. 6-5c, d). Thus, the exchange sites were homogeneous in the Oxisol. The main components capable of cation exchange at

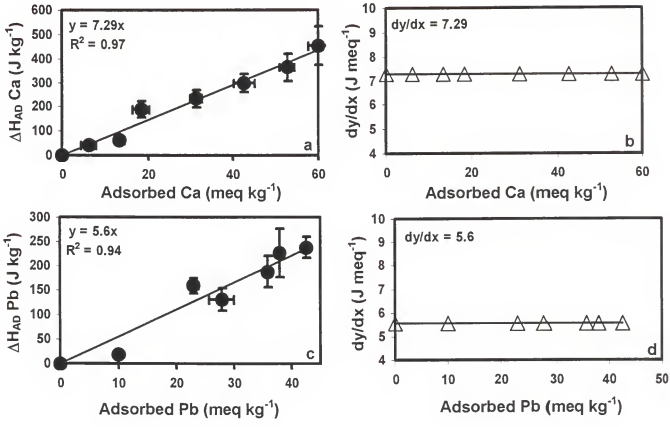

Figure 6-5. Integral heats of adsorption (ΔH_{AD}) for a) Oxisol-Ca and c) Oxisol-Pb as well as differential heats of adsorption for b) Oxisol-Ca and d) Oxisol-Pb.

the pH of the experiment (pH = 4.7) were organic matter and kaolinite (PZCs < 3 and ≈ 3 to 5; respectively; Braggs et al., 1994; Ferris and Jepson, 1975; Sparks, 1995). Both materials have external cation exchange sites with similar affinity for K^+. This most likely is due to their relatively strong field strength compared to most soil colloids (McBride, 1994; Thompson et al., 1989). The only other components capable of ion exchange in this soil were gibbsite and goethite which would be positively charged at pH 4.7 and, thus, incapable of cation exchange (PZCs of gibbsite and goethite ≈ 5 to 9 and 7.8 to 9, respectively; Sparks, 1995; Su and Suarez, 1997).

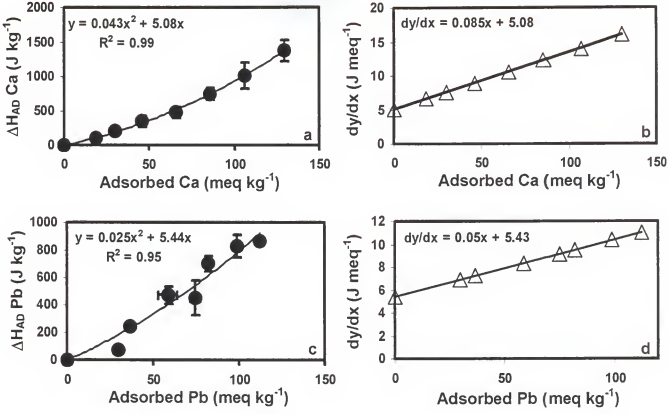

Figure 6-6. Integral heats of adsorption (ΔH_{AD}) for a) Ultisol-Ca and c) Ultisol-Pb as well as differential heats of adsorption for b) Ultisol-Ca and d) Ultisol-Pb.

The Ultisol exhibited a different trend (Fig. 6-6). The differential plots for Ca^{2+} and Pb^{2+} yielded straight lines with slightly increasing slopes. There was a 0.09 and 0.05 increase in ΔH for every 1 equivalent increase in adsorbed metal for Ca^{2+} and Pb^{2+}, respectively; Figs. 6-6c, d. The exchange sites in this soil show evidence for heterogeneity. It took an increasing amount of energy to remove adsorbed K^{+} as the quantity of this metal cation decreased on the exchanger.

The important difference between this soil and the Oxisol is the presence of interstratified smectite (Table 4-1; pg. 50). The Ultisol had ≈ 17 % smectite in the clay

fraction. As previously indicated, 2:1 layer silicates generally exhibit high selectivity for K^+ in their interlayers. Therefore, the data suggests that the Ca^{2+} and Pb^{2+} initially replaced K^+ adsorbed to external exchange sites (i.e. organic matter, kaolinite, edges and planar smectitic surfaces) then proceeded to replace K^+ from the smectite interlayers which required more energy (Gast, 1972; Sparks and Jardine, 1981).

X-ray diffraction confirmed Ca^{2+}, and presumably Pb^{2+}, was able to replace interlayer K^+. Ceramic tiles were covered with the < 2 μm fraction of this soil and saturated with Ca^{2+}, K^+, then Ca^{2+}. The d-spacings, of the smectite peak, were measured at each interval/saturation. The two Ca^{2+}-saturations gave similar d-spacings ($\approx$ 14.72 Å) while the d-spacing under K^+-saturation was $\approx$ 14.04 Å.

Conclusions

Data collected from sorption isotherm studies enabled a better understanding of K/Ca and K/Pb interactions in two highly weathered tropical soils from Puerto Rico (Oxisol and Ultisol). Gaines-Thomas selectivity coefficients were calculated for a range of K/Ca and K/Pb ratios on soil exchange sites. The soils exhibited a preference for K^+ over Ca^{2+} or Pb^{2+} at all ratios of K^+ on the exchanger. Kaolinite, which was abundant in the Oxisol and Ultisol, has high selectivity for K^+ due to its relatively high charge density and K^+s low hydration energy. This explained our soils' high affinity for K^+.

Soil composition played a larger role than metal type in the patterns of selectivity for the cations studied. Selectivity for Ca^{2+} and Pb^{2+} stayed the same in the Oxisol and increased in the Ultisol with increasing concentrations of Ca^{2+} or Pb^{2+} on the exchanger. The Oxisol was composed entirely of colloids having external surface exchange sites

while the Ultisol possessed some smectitic material (17 %). The interlayers of 2:1 layer silicates have been shown to have high affinity for K^+. This is probably why the selectivity for Ca^{2+} and Pb^{2+} decreased with increasing divalent metal saturation in the Ultisol.

Flow calorimetry enabled the direct measurement of the enthalpy change associated with cation exchange reactions in our soils. The enthalpy change provides information about the binding strength of a cationic species to/on soil surfaces. The adsorption of Ca^{2+} and Pb^{2+} when replacing K^+ was endothermic. The ΔH was less for Pb^{2+} adsorption than that for Ca^{2+} on both soils. This means that it took more energy for Ca^{2+} rather than Pb^{2+} to replace K^+ from soil surfaces. Also, due to the presence of smectite in the Ultisol's clay fraction and its high affinity for K^+ in the interlayer, it took more energy for the divalent metals to replace K^+ in this soil than in the Oxisol.

Lead was irreversibly sorbed at all concentration steps in both soils. The Oxisol had between $\approx$ 3000 and 3500 ppm nonexchangeable Pb while that value in the Ultisol was significantly less at $\approx$ 1900 ppm. The Oxisol had more organic matter and Fe/Al oxides than the Ultisol and accounted for the greater irreversible Pb sorption in the former soil. The SEM-EDX was used to identify Pb phases on the soil surfaces in order to elucidate the nature of Pb binding to our soils. The data suggested chemisorption was the dominant mechanism of irreversible Pb sorption. There were discrete Pb-C phases detected in both soils where the C was from organic matter. Soil solutions were undersaturated with respect to solid phase $Pb(OH)_2$ and $Pb(CO_3)_2$ formation ruling out precipitation as a retention mechanism for Pb.

Lead chemisorption was found to be driven predominantly by a change in entropy in our soil-metal systems as there was no detectable heat effect associated with this reaction. This is possible as the loss of Pb^{2+} from solution and its replacement by H^+, OH^-, or H_2O, potential soil surface leaving groups, would result in a positive solution entropy change. This would provide an increased driving force for this reaction.

In agreement with the selectivity data, the determination of surface heterogeneity indicated that the energetics of Pb^{2+} and Ca^{2+} adsorption were more dependent on soil composition than metal type. As divalent metal saturation on the Oxisol increased, there was no change in the heat required to replace the remaining K^+. This indicated exchange sites were homogeneous in this soil. However, it took an increasing amount of energy to remove adsorbed K^+ as the quantity of this metal decreased on the exchanger in the Ultisol soil. Thus, there were exchange sites in this soil having differing affinities for the metals we studied. The differences were due to soil properties and were specifically related to the presence of smectite in the Ultisol and its absence in the Oxisol.

The data collected in the sorption isotherm study coupled with information obtained by the flow calorimeter enabled improved understanding of surface sorption reactions involving Ca^{2+}, K^+, and Pb^{2+} and tropical soil surfaces. Depending on heavy metal soil contamination levels as well as soil properties, Pb^{2+} and other heavy metals may occupy a fraction to a significant portion of soil cation exchange sites. Therefore, understanding how the enthalpy of adsorption of a particular heavy metal changes with its surface coverage is important in elucidating how available this metal will be to plant/animal uptake as well as its mobility and stability in the soil environment.

CHAPTER 7
CONCLUSIONS

The results obtained from the experiments investigating soil surface charge and soil surface charge effects on Cd and Pb sorption in tropical soils provided insights about the important soil factors contributing to metal retention by these types of soils. The point of zero charge is one of the most important parameters used to describe variable-charge surfaces. The three methods used, potentiometric titration, ion adsorption, and electroacoustic mobility, measure theoretically different types of charge. Comparisons of the points of zero charge ascertained for mineral standard kaolinite and synthetic goethite by each of these methods with literature values fell within the ranges of those reported. Furthermore, the points of zero charge for the soils gave consistent values suggesting the three methods accurately measured their surface charge. This was especially noteworthy and encouraging for the determination of the IEP via electroacoustic mobility, performed by the AcoustoSizer™. The time required to generate this value was drastically reduced compared the points of zero charge found via potentiometric titration or ion adsorption methods.

The results from the batch studies looking at Cd and Pb sorption in tropical soils as a function of metal concentration, solution pH, and surface charge indicated a greater affinity of Pb for soil sorption sites compared to Cd. Soil pH had a larger effect on Cd sorption than on Pb sorption. Metal type was more important than soil composition for the sorption of either Cd or Pb in the soils investigated. Furthermore, plots of negative

surface charge and sorbed Cd or Pb vs. soil pH suggested Pb was sorbed through both inner- and outer-sphere reactions while Cd was mainly retained via electrostatic reactions, especially at low pH. The preference for Pb sorption over Cd sorption exhibited by these soils was most likely due to these metals' chemical properties (e.g. Pb has a higher electronegativity, lower pK_H, and higher hydrated charge density than Cd).

The study of the sequential sorption of Cd and Pb by the tropical soils enabled determination of how these metals interact when introduced to soils at different times, the specificity soil sorption sites exhibit for one metal over another, and provided evidence for sorption mechanisms. Similar to the previous study, Pb was sorbed in preference to Cd regardless of the order in which it entered soil systems. However, when Cd was introduced to soils prior to Pb, more of it was retained at high affinity/nonexchangeable sites relative to the opposite scenario. Lead was much less exchangeable than Cd and ratios of nonexchangeable Pb to nonexchangeable Cd followed the trend Oxisol > Ultisol > Mollisol. This was opposite the trend of soil CEC but the same trend as the proportion of variable-charge colloids, which were abundant in the Oxisol. Also, the data suggested that the irreversible sorption of Cd or Pb occurred at different sites from those of exchange, as soil CEC remained constant throughout the experiments.

The determination of selectivity as well as the enthalpy change or K/Ca and K/Pb exchange and sorption reactions in the Oxisol and Ultisol indicated the importance of soil type. Selectivity coefficients and surface heterogeneity determination for Ca and Pb stayed the same in the Oxisol and decreased in the Ultisol with increasing surface coverage of these ions. This was because the Oxisol was composed entirely of colloids having external surface exchange sites while the Ultisol possessed some smectitic

material. The interlayers of 2:1 minerals have high affinities for K which is probably why selectivity decreased and the differential enthalpy change of divalent metal adsorption increased with increasing surface coverage of Ca or Pb. The results suggest Pb chemisorption was largely driven by a change in entropy as their was no detectable heat effect associated with this reaction. This is possible as Pb chemisorption would bring about an increase in solution entropy.

The batch studies considering Cd and Pb sorption as a function of concentration, pH, surface charge, and sequence of metal addition emphasized the importance of metal type relative to soil composition in ascertaining reactivities of these metals with the soils studied. On the other hand, the selectivity and thermodynamic column studies demonstrated soil composition was the main factor/predictor of metal behavior in the tropical soils studied. The batch sorption studies were black-box experiments where any reaction involving metal retention by soils was deemed sorption. Thus, the chemical properties of the metals were paramount. The column selectivity and thermodynamic studies, however, mainly focused on cation exchange and measured selectivity and enthalpy changes derived only from exchange data. It follows that the patterns of cation exchange were, consequently, dominated by differences in soil properties as opposed to differences in the electrostatic chemical properties of two divalent cations, Ca and Pb.

Each of the studies involving Cd and Pb indicated tropical soil surfaces had a much higher affinity for Pb. Therefore, Pb presents a lower hazard than Cd in terms of mobility and bioavailability in these soil systems. This has implications for groundwater contamination and regulatory issues involving these metals in tropical environments.

The assumption that highly weathered tropical soils have low affinities for heavy metals (e.g. Cd and Pb), due to their low surface charge densities, did not hold true for Pb in our studies. Our results showed the Oxisol and Ultisol soils were able to retain large quantities of this metal. Furthermore, Oxisols and Ultisols in the field may have soil depths exceeding 10 m. Thus, even if leaching were a factor, these soils possess adequate sites for strong binding of Pb throughout the soil profile.

LIST OF REFERENCES

Adriano, D.C. 1986. Trace elements in the terrestrial environment. Springer-Verlag, New York, NY.

Ahmed, S., S. Chughtai and M.A. Keane. 1998. The removal of cadmium and lead from aqueous solution by ion exchange with Na-Y zeolite. Sep. Purif. Technol. 13:57-64.

Ainsworth, C.C., J.L. Pilon, P.L. Gassman and W.G. van der Sluys. 1994. Cobalt, cadmium, and lead sorption to hydrous iron oxide: Residence time effect. Soil Sci. Soc. Am. J. 58:1615-1623.

Airoldi, C. and S.A.M. Critter. 1997. Brazilian red Latosol a typic soil as an exchanger: A thermodynamic study involving Cu, Zn, Cd, Hg, Pb, Ca and Na. Clay Clay Min. 45:125-131.

Alloway, B.J. 1990a. The origins of heavy metals in soils. p. 29-39. *In* B.J. Alloway (ed.) Heavy metals in soils. John Wiley and Sons, Inc., New York, NY.

Alloway, B.J. 1990b. Soil processes and the behavior of metals. p. 7-28. *In* B.J. Alloway (ed.) Heavy metals in soils. John Wiley and Sons, Inc., New York, NY.

Altin, O., O.H. Ozbelge and T. Dogu. 1999. Effect of pH, flow rate and concentration on the sorption of Pb and Cd on montmorillonite: I. Experimental. J. Chem. Technol. Biotechnol. 74:1131-1138.

Angelone, M. and C. Bini. 1992. Trace element concentrations in soils and plants of western Europe. p. 19-60. *In* D.C. Adriano (ed.) Biogeochemistry of trace elements. CRC Press, Boca Raton, FL.

Atkinson, R.J., A.M. Posner and J.P. Quirk. 1967. Adsorption of potential-determining ions at the ferric oxide-aqueous electrolyte interface. J. Phys. Chem. 71:550-558.

Balistrieri, L.S. and J.W. Murray. 1981. The surface chemistry of goethite (FeOOH) in major ion seawater. Am. J. Sci. 281:788-806.

Balistrieri, L.S. and J.W. Murray. 1982. The adsorption of Cu Pb, Zn, and Cd on goethite from major ion seawater. Geochim. Cosmochim. Acta 46:1253-1265.

Barbarick, K.A., J.A. Ippolito and D.G. Westfall. 1998. Extractable trace elements in the soil profile after years of biosolids application. J. Environ. Qual. 27:801-805.

Bargar, J.R., G.E. Brown and G.A. Parks. 1997a. Surface complexation of Pb (II) at oxide-water interfaces: I. XAFS and bond-valence determination of mononuclear and polynuclear Pb (II) sorption products on aluminum oxides. Geochim. Cosmochim. Acta 61:2617-2637.

Bargar, J.R., G.E. Brown and G.A. Parks. 1997b. Surface complexation of Pb (II) at oxide-water interfaces: II. XAFS and bond-valence determination of mononuclear Pb (II) sorption products and surface functional groups on iron oxides. Geochim. Cosmochim. Acta 61:2639-2652.

Bargar, J.R., G.E. Brown and G.A. Parks. 1998. Surface complexation of Pb(II) at oxide-water interfaces: III. XAFS determination of Pb(II) and Pb(II)-chloro complexes on goethite and alumina. Geochim. Cosmochim. Acta 62:193-207.

Barrer, R.M., D.J. Ward and L.V.C. Rees. 1963. Thermochemistry and thermodynamics of ion exchange in a crystalline exchange medium. Proc. R. Soc. London Ser. A-Math 273:180-197.

Barrow, N.J. 1987. Reactions with variable charge soil. Fert. Res. 14:1-100.

Basta, N.T., D.J. Pantone and M.A. Tabatabai. 1993. Path-analysis of heavy-metal adsorption by soil. Agron. J. 85:1054-1057.

Benjamin, M.M. and J.O. Leckie. 1981a. Competitive adsorption of Cd, Cu, Zn, and Pb on amorphous iron oxyhydroxide. J. Colloid Interface Sci. 83:410-419.

Benjamin, M.M. and J.O. Leckie. 1981b. Multi-site adsorption of Cd, Cu, Zn, and Pb on amorphous iron oxyhydroxide. J. Colloid Interface Sci. 79:209-211.

Bibak, A. 1994. Cobalt, copper, and manganese adsorption by aluminum- and iron-oxides and humic-acid. Commun. Soil Sci. Plant Anal. 25:3229-3239.

Bingham, F.T., G. Sposito and J.E. Strong. 1984. The effect of chloride on the availability of cadmium. J. Environ. Qual. 13:71-74.

Bleam, W. and M.B. McBride. 1984. Cluster formation versus isolated-site adsorption. A study of Mn(II) and Mg(II) adsorption on boehmite and goethite. J. Colloid Interface Sci. 103:124-132.

Boekhold, A.E., E. Temminghoff and S. van der Zee. 1993. Influence of electrolyte composition and pH on cadmium sorption by an acid sandy soil. J. Soil Sci. 44:85-96.

Boruvka, L., S. Kristoufkova, J. Kozak and C. HuanWei. 1997. Speciation of cadmium, lead and zinc in heavily polluted soils. Rostl. Vyroba 43:187-192.

Brady, P.V., R.T. Cygan and K.L. Nagy. 1996. Molecular controls on kaolinite surface charge. J. Colloid Interface Sci. 183:356-364.

Braggs, B., D. Fornasiero, J. Ralston and R.S. Smart. 1994. The effect of surface modification by an organosilane on the electrochemical properties of kaolinite. Clays Clay Miner. 42:123-136.

Brendecke, J.W. and I.L. Pepper. 1996. The extent of global pollution. p. 3-8. *In* I.L. Pepper, C.P. Gerba and M.L. Brusseau (eds.) Pollution science. Academic Press, San Diego, CA.

Brown, G.E., A.L. Foster and J.D. Ostergren. 1999. Mineral surfaces and bioavailability of heavy metals: A molecular-scale perspective. Proc. Natl. Acad. Sci. 96:3388-3395.

Bruemmer, G., K.G. Tiller, U. Herms and P.M. Clayton. 1983. Adsorption-desorption and/or precipitation-dissolution processes of zinc in soils. Geoderma 31:337-354.

Bruemmer, G.W., J. Gerth and U. Herms. 1986. Heavy metal species, mobility and availability in soils. Z. Planzenernaehr. Bodenkd. 149:382-398.

Bruemmer, G.W., J. Gerth and K.G. Tiller. 1988. Reaction kinetics of the adsorption and desorption of nickel, zinc, and cadmium by goethite. I. Adsorption and diffusion of metals. J. Soil Sci. 39:37-52.

Carroll-Webb, S.A. and J.V. Walther. 1988. A surface complex reaction model for the pH-dependence of corundum and kaolinite dissolution rates. Geochim. Cosmochim. Acta 52:2609-2623.

Chang, A.C., J.E. Wernicke, A.L. Page and L.J. Lund. 1984. Accumulation of heavy metals in sewage-sludge-treated soils. J. Environ. Qual. 13:87-91.

Charlet, L. and G. Sposito. 1987. Monovalent ion adsorption by an Oxisol. Soil Sci. Soc. Am. J. 51:1155-1160.

Chen, M. and L.Q. Ma. 1998. Comparison of four USEPA methods for trace metal analysis using certified and Florida soils. J. Environ. Qual. 27:1294-1300.

Chorover, J. and G. Sposito. 1995. Surface charge characteristics of kaolinitic tropical soils. Geochim. Cosmochim. Acta 59:875-884.

Colloidal Dynamics. 1996. AcoustoSizer Users Manual. Colloidal Dynamics, Inc., Warwick, RI.

Coughlin, B.R. and A.T. Stone. 1995. Nonreversible adsorption of divalent metal ions (Mn^{II}, Co^{II}, Ni^{II}, Cu^{II}, and Pb^{II}) onto goethite: Effects of acidification, Fe^{II} addition, and picolinic acid addition. Environ. Sci. Technol. 29:2445-2455.

Coulter, B.S. 1969. The chemistry of hydrogen and aluminum ions in soils, clay minerals, and resins. Soils Fert. 32:215-223.

Dalang, F., J. Buffle and W. Haerdl. 1984. Study of the influence of fulvic substances on the adsorption of copper(II) ions at the kaolinite surface. Environ. Sci. Technol. 18:135-141.

Davies, B.E. 1992. Trace metals in the environment: Retrospect and prospect. p. 1-18. *In* D.C. Adriano (ed.) Biogeochemistry of trace metals. Lewis Publ., Boca Raton, FL.

Davis, J.A. and D.B. Kent. 1990. Surface complexation modeling in aqueous geochemistry. p. 177-260. *In* J. M.F. Hochella and A.F. White (eds.) Reviews in mineralogy. 23: Mineral-water interface geochemistry. Mineralogical Society of America, Washington, DC.

Davis, J.A. and J.O. Leckie. 1978. Surface ionization and complexation at the oxide/water interface. II. Surface properties of amorphous iron oxyhydroxide and adsorption of metals. J. Colloid Interface Sci. 67:90-107.

de Haan, F.A.M. and W.H. van Riemsdijk. 1985. Behavior of inorganic contaminants in soil. p. 19-32. *In* J.W. Assink and W.J. van der Brink (eds.) Contaminated soil. Martinus Nijhoff Publ., Boston, MA.

Deist, J. and O. Talibudeen. 1967. Thermodynamics of K-Ca exchange in soils. J. Soil Sci. 18:138-148.

Djafer, M., R.K. Khandal and M. Terce. 1991. Interactions between different anions and the goethite surface as seen by different methods. Colloids Surfaces 54:209-218.

Domask, W.C. and K.A. Kobe. 1952. Mercurimetric determination of chlorides and water-soluble chlorohydrins. Anal. Chem. 24:989.

Doner, H.E. 1978. Chloride as a factor in mobilities of Ni(II), Cu(II), and Cd(II) in soil. Soil Sci. Soc. Am. J. 42:882-885.

Echeverria, J.C., M.T. Morera, C. Mazkiaran and J.J. Garrido. 1998. Competitive sorption of heavy metal by soils. Isotherms and fractional factorial experiments. Environ. Pollut. 101:275-284.

Eick, M.J., J.D. Peak, P.V. Brady and J.D. Pesek. 1999. Kinetics of lead adsorption/desorption on goethite: Residence time effect. Soil Sci. 164:28-39.

Elkhatib, E.A., G.M. Elshebiny, G.M. Elsubruiti and A.M. Balba. 1993. Thermodynamics of lead sorption and desorption in soils. Z. Pflanzenernaehr. Bodenk. 156:461-465.

Ferris, A.P. and W.B. Jepson. 1975. The exchange capacities of kaolinite and the preparation of homoionic clays. J. Colloid Interface Sci. 51:245-259.

Filius, A., T. Streck and J. Richter. 1998. Cadmium sorption and desorption in limed topsoils as influenced by pH: Isotherms and simulated leaching. J. Environ. Qual. 27:12-18.

Findlay, A.D., D.W. Thompson and E. Tipping. 1996. Electrokinetic properties of oxide particles in natural waters. Colloids Surfaces 111:203-212.

Forbes, E.A., A.M. Posner and J.P. Quirk. 1976. The specific adsorption of divalent Cd, Co, Cu, Pb, and Zn on goethite. J. Soil Sci. 27:154-166.

Forstner, U. 1995. Land contamination by metals - Global scope and magnitude of problem. p. 1-34. *In* H.E. Allen, C.P. Huang, G.W. Bailey and A.R. Bowers (eds.) Metal speciation and contamination of soil. CRC Press, Inc., Boca Raton, FL.

Foscolos, A.E. and I. Barshad. 1969. Equilibrium constants between freshly prepared and aged H montmorillonites and chloride salt solutions. Soil Sci. Soc. Am. Proc. 33:242-247.

Fox, R.L. 1982. Some highly weathered soils of Puerto Rico, 3. Chemical properties. Geoderma 27:139-176.

Gallez, A., A. Juo and A. Herbillon. 1976. Surface and charge characteristics of selected soils in the tropics. Soil Sci. Soc. Am. J. 40:601-608.

Gao, S.A., W.J. Walker, R.A. Dahlgren and J. Bold. 1997. Simultaneous sorption of Cd, Cu, Ni, Zn, Pb, and Cr on soils treated with sewage sludge supernatant. Water Air Soil Pollut. 93:331-345.

Gast, R.G. 1972. Alkali metal cation exchange on Chambers montmorillonite. Soil Sci. Soc. Am. Proc. 36:14-19.

Gast, R.G., R.V. Bladel and K.B. Deshpande. 1969. Standard heats and entropies of exchange for alkali metal cations on Wyoming bentonite. Soil Sci. Soc. Am. Proc. 33:661-664.

Gee, G.W. and J.W. Bauder. 1986. Particle-size analysis. p. 383-411. *In* A. Klute (ed.) Part 1: Methods of soil analysis. Physical and mineralogical methods. SSSA, Inc., Madison, WI.

Gillman, G.P. and L.C. Bell. 1978. Soil solution studies on weathered soils from tropical North Queensland. Aust. J. Soil Res. 16:67-77.

Gomes, P.C., M. Fontes, A.G. da Silva, E.de S. Mendonca and A.R. Netto. 2001. Selectivity sequence and competitive adsorption of heavy metals by Brazilian soils. Soil Sci. Soc. Am J. 65:1115-1121.

Gong, C. and R.J. Donahoe. 1997a. An experimental study of heavy metal attenuation and mobility in sandy loam soils. Appl. Geochem. 12:243-254.

Gong, C.R. and R.J. Donahoe. 1997b. An experimental study of heavy metal attenuation and mobility in sandy loam soils. Appl. Geochem. 12:243-254.

Goulding, K. 1983. Thermodynamics and potassium exchange in soils and clay minerals. p. 215-264. *In* N.C. Brady (ed.) Advances in agronomy. vol. 36. Academic Press, Inc., New York, NY.

Goulding, K.W.T. and O. Talibudeen. 1984. Thermodynamics of K-Ca exchange in soils. II. Effects of mineralogy, residual K and pH in soils from long-term adas experiments. J. Soil Sci. 35:409-420.

Gunneriusson, L. 1994. Composition and stability of Cd(II)-chloro and Cd(II)-hydroxo complexes at the goethite (Alpha-FeOOH) water interface. J. Colloid Interface Sci. 163:484-492.

Gunneriusson, L., L. Lovgren and S. Sjoberg. 1994. Complexation of Pb(II) at the goethite (FeOOH)/water interface: The influence of chloride. Geochim. Cosmochim. Acta 58:4973-4983.

Gustafsson, J.P. 2000. Visual Minteq [Online]. Available at http://amov.ce.kth.se/PEOPLE/Gustafjp/vminteq.htm (verified 20 Nov. 2001)

Haas, C.N. and N.D. Horowitz. 1986. Adsorption of cadmium to kaolinite in the presence of organic material. Water Air Soil Pollut. 27:131-140.

Hanafi, M.M. and G.J. Maria. 1998. Cadmium and zinc in acid tropical soils: III. Response of cocoa seedlings in a greenhouse experiment. Commun. Soil Sci. Plant Anal. 29:1949-1960.

Hanafi, M.M. and J. Sjiaola. 1998. Cadmium and zinc in acid tropical soils: I. Soil physicochemical properties effect on their adsorption. Commun. Soil Sci. Plant Anal. 29:1919-1931.

Hansen, A.M. and P. Maya. 1997. Adsorption-desorption behaviors of Pb and Cd in Lake Chapala, Mexico. Environ. Int. 23:553-564.

Helfferich, F. 1962. Ion exchange. McGraw-Hill Book Co., Inc., New York, NY.

Hendershot, W.H. and L.M. Lavkulich. 1983. Effect of sesquioxide coatings on surface charge of standard mineral and soil samples. Soil Sci. Soc. Am. J. 47:1252-1260.

Hong, J.H. and P.N. Pintauro. 1996. Selective removal of heavy metals from contaminated kaolin by chelators. Water Air Soil Pollut. 87:73-91.

Hooda, P.S. and B.J. Alloway. 1994. Sorption of Cd and Pb by selected temperate and semiarid soils - Effects of sludge application and aging of sludged soils. Water Air Soil Pollut. 74:235-250.

Hooda, P.S. and B.J. Alloway. 1998. Cadmium and lead sorption behaviour of selected English and Indian soils. Geoderma 84:121-134.

Hrudey, S.E., W. Chen and C.G. Rousseaux. 1995. Bioavailability in environmental risk assessment. Lewis Publ., Boca Raton, FL.

Hue, N.V. and S.A. Ranjith. 1993. Sewage sludges in Hawaii: Chemical composition and reactions with soils and plants. Water Air Soil Pollut. 72:265-283.

Huheey, J.E. 1983. Inorganic chemistry: Principles of structure and reactivity. 3rd ed. Harper and Row, Publ., San Francisco, CA.

Hyun, H., A.C. Chang, D.R. Parker and A.L. Page. 1998. Cd solubility and phytoavailability in sludge-treated soil: Effects of soil organic carbon. J. Environ. Qual. 27:329-334.

Jang, A., Y.S. Choi and I.S. Kim. 1998. Batch and column tests for the development of an immobilization technology for toxic heavy metals in contaminated soils of closed mines. Wat. Sci. Tech. 37:81-88.

Jenne, E.A. 1968. Controls on Mn, Fe, Co, Ni, Cu, and Zn concentrations in soils and waters – The dominant role of hydrous manganese and iron oxides. Adv. Chem. Ser. 73:337-387.

Jensen, D.L., P.E. Holm and T.H. Christensen. 2000. Soil and groundwater contamination with heavy metals at two scrap iron and metal recycling facilities. Waste Manage. Res. 18:52-63.

Johnson, C.E. and R.J. Petras. 1998. Distribution of zinc and lead fractions within a forest Spodosol. Soil Sci. Soc. Am. J. 62:782-789.

Jordan, M.J. and M.P. LeChevalier. 1975. Effects of zinc-smelter emissions on forest soil microflora. Can. J. Microbiol. 21:1855-1865.

Juo, A. and S.A. Barber. 1969. An explanation for the variability in Sr-Ca exchange selectivity of soils, clays, and humic acid. Soil Sci. Soc. Am. Proc. 33:360-363.

Kabala, C. and B.R. Singh. 2001. Fractionation and mobility of copper, lead, and zinc in soil profiles in the vicinity of a copper smelter. J. Environ. Qual. 30:485-492.

Kabata-Pendias, A. and H. Pendias. 1992. Trace elements in soils and plants. 2nd ed. CRC Press, Boca Raton, FL.

Keng, J. and G. Uehara. 1974. Chemistry, mineralogy, and taxonomy of Oxisols and Ultisols. Florida Crop Sci. Proc. 33:119-126.

Kinneburgh, D.G., M.L. Jackson and J.K. Sayers. 1976. Adsorption of alkaline earth, transition and heavy metal cations by hydrous oxide gels of iron and aluminum. Soil Sci. Soc. Am. J. 40:796-799.

Krebs, R., S.K. Gupta, G. Furrer and R. Schulin. 1998. Solubility and plant uptake of metals with and without liming of sludge-amended soils. J. Environ. Qual. 27:18-23.

Laudelot, H., R.V. Bladel, G.H. Bolt and A.L. Page. 1968. Thermodynamics of heterovalent cation exchange reactions in a montmorillonite clay. Trans. Far. Soc. 64:1477-1488.

Lavardiere, M.R. and R.M. Weaver. 1977. Charge characteristics of spodic horizons. Soil Sci. Soc. Am. J. 41:505-510.

Levy, G.J., H. van der Watt, I. Shainberg and H. du Pleiss. 1988. Potassium-calcium and sodium-calcium exchange on kaolinite and kaolinitic soils. Soil Sci. Soc. Am. J. 52:1259-1264.

Levy, R. and D. Hillel. 1968. Thermodynamic equilibrium constants of sodium-calcium exchange in some Israel soils. Soil Sci. 106:393-398.

Lewis-Russ, A. 1991. Measurement of surface charge of inorganic geologic materials: Techniques and their consequences. p. 199-243. *In* D.L. Sparks (ed.) Advances in Agronomy. 46. Academic Press, Inc., Boston, MA.

Lim, T.T., J.H. Tay and C.I. Teh. 1997. Sorption and speciation of heavy metals from incinerator fly ash in a marine clay. J. Environ. Eng.-ASCE 123:1107-1115.

Lindsay, W.L. 1979. Chemical equilibria in soils. John Wiley and Sons, New York, NY.

Lopez, F.A., C. Perez, E. Sainz and M. Alonso. 1995. Adsorption of Pb2+ on blast-furnace sludge. J. Chem. Technol. Biotechnol. 62:200-206.

Lopez-Delgado, A., C. Perez and F.A. Lopez. 1998. Sorption of heavy metals on blast furnace sludge. Water Res. 32:989-996.

Ma, L.Q. 1996. Factors influencing the effectiveness and stability of aqueous lead immobilization by hydroxyapatite. J. Environ. Qual. 25:1420-1429.

Ma, L.Q. and G.N. Rao. 1997. Effects of phosphate rock on sequential chemical extraction of lead in contaminated soils. J. Environ. Qual. 26:788-794.

Ma, Q.Y., S.J. Traina and T.J. Logan. 1994a. Effects of aqueous Al, Cd, Cu, Fe(II), Ni, and Zn on Pb immobilization by hydroxyapatite. Environ. Sci. Technol. 28:1219-1228.

Ma, Q.Y., T.J. Logan and S.J. Traina. 1994b. Effects of NO_3^-, Cl^-, F^-, SO_4^{2-}, and CO_3^{2-} on Pb^{2+} immobilization by hydroxyapatite. Environ. Sci. Technol. 28:408-418.

Ma, Q.Y., T.J. Logan and S.J. Traina. 1995. Lead immobilization from aqueous solutions and contaminated soils using phosphate rocks. Environ. Sci. Technol. 29:1118-1126.

Maes, A. and A. Cremers. 1977. Charge density effects in ion exchange. Part 1. Heterovalent exchange equilibria. J. Chem. Soc. Far. I 73:1807-1814.

Majone, M., M.P. Papini and E. Rolle. 1998. Influence of metal speciation in landfill leachates on kaolinite sorption. Water Res. 32:882-890.

Manahan, S.E. 1990. Hazardous waste chemistry, toxicology and treatment. Lewis Publ., Inc., Chelsea, MI.

Marcano-Martinez, E. and M.B. McBride. 1989. Comparison of the titration and ion adsorption methods for surface charge measurements in Oxisols. Soil Sci. Soc. Am. J. 53:1040-1045.

Matis, K.A., A.I. Zouboulis, D. Zamboulis and A.V. Valtadorou. 1999. Sorption of As(V) by goethite particles and study of their flocculation. Water Air Soil Pollut. 111:297-316.

McBride, M.B. 1989. Reactions controlling heavy metal solubility in soils. Adv. Soil Sci. 10:1-57.

McBride, M.B. 1994. Environmental chemistry in soils. Oxford University Press, Oxford, England.

McKenzie, R.M. 1980. The adsorption of lead and other heavy metals on oxides of manganese and iron. Aust. J. Soil Res. 18:61-73.

McLaren, R.G., R. Naidu, J. Smith and K.G. Tiller. 1998. Fractionation and distribution of arsenic in soils contaminated by cattle dip. J. Environ. Qual. 27:348-354.

Mehra, O.P. and M.L. Jackson. 1960. Iron oxide removal from soils and clays by a dithionite-citrate system buffered with sodium bicarbonate. Clays Clay Miner. 8:317-327.

Mekaru, T. and G. Uehara. 1972. Anion adsorption in ferruginous tropical soils. Soil Sci. Soc. Am. Proc. 36:296-300.

Merrington, G. and B.J. Alloway. 1994. The flux of Cd, Cu, Pb and Zn in mining polluted soils. Water Air Soil Pollut. 73:333-344.

Merrington, G. and B.J. Alloway. 1997. Determination of the residual metal binding characteristics of soils polluted by Cd and Pb. Water Air Soil Pollut. 100:49-62.

Morais, F.I., A.L. Page and L.J. Lund. 1976. The effect of pH, salt concentration, and nature of electrolytes on the charge characteristics of Brazilian tropical soils. Soil Sci. Soc. Am. J. 40:521-527.

Moreira, J.C. 1996. Threats by heavy metals: Human and environmental contamination in Brazil. Sci. Total Environ. 188:S61-S71.

Motta, M.M. and C.F. Miranda. 1989. Molybdate adsorption on kaolinite, montmorillonite, and illite: Constant capacitance modeling. Soil Sci. Soc. Am. J. 53:380-385.

Naidu, R., N.S. Bolan, R.S. Kookana and K.G. Tiller. 1994. Ionic-strength and pH effects on the sorption of cadmium and the surface charge of soils. Eur. J. Soil Sci. 45:419-429.

Naidu, R., R.S. Kookana, M.E. Sumner, R.D. Harter and K.G. Tiller. 1997. Cadmium sorption and transport in variable charge soils: A review. J. Environ. Qual. 26:602-617.

Naidu, R., M.E. Sumner and R.D. Harter. 1998. Sorption of heavy metals in strongly weathered soils: An overview. Environ. Geochem. Health 20:5-9.

Nakhone, L.N. 1997. Cadmium adsorption and desorption on humic acid, montmorillonite, goethite, kaolinite and calcareous clay. Discov. Innov. 9:53-71.

Nelson, D.W. and L.E. Sommers. 1996. Total carbon, organic carbon and organic matter. p. 961-1010. *In* D.L. Sparks (ed.) Part 3: Methods of soil analysis. Chemical methods. SSSA, Inc., Madison, WI.

Nightingale, E.R. 1959. Phenomenological theory of ion solution. Effective radii of hydrated cations. J. Phys. Chem. 63:1381-1387.

Nriagu, J.O. 1998. Paleoenvironmental research – Tales told in lead. Sci. 281:1622-1623.

O'Brien, R.W., D.W. Cannon and W.N. Rowlands. 1995. Electroacoustic determination of particle size and zeta potential. J. Colloid Interface Sci 173:406-418.

O'Brien, R.W. and W.N. Rowlands. 1993. Measuring the surface conductance of kaolinitic particles. J. Colloid Interface Sci. 159:471-476.

Ogwada, R.A. and D.L. Sparks. 1986. A critical-evaluation on the use of kinetics for determining thermodynamics of ion-exchange in soils. Soil Sci. Soc. Am. J. 50:300-305.

Page, A.L., F.T. Bingham, T.J. Granje and M.J. Garber. 1963. Availability and fixation of added potassium in two California soils when cropped to cotton. Soil Sci. Soc. Am. Proc. 27:323-326.

Page, A.L., W.D. Burge, T.J. Granje and M.J. Garber. 1967. Potassium and ammonium fixation in vermiculite soils. Soil Sci. Soc. Am. Proc. 31:337-341.

Pardo, M.T. 2000. Sorption of lead, copper, zinc, and cadmium by soils: Effect of nitriloacetic acid on metal retention. Commun. Soil Sci. Plant Anal. 31:31-40.

Parida, K., P.K. Satapathy and N. Das. 1996. Studies on Indian Ocean manganese nodules. 4. Adsorption of some bivalent heavy metal ions onto ferromanganese nodules. J. Colloid Interface Sci. 181:456-462.

Parker, J.C., L.W. Zelazny, S. Samprath and W.G. Harris. 1979. A critical evaluation of the extension of zero point of charge (zpc) theory to soil systems. Soil Sci. Soc. Am. J. 43:668-674.

Parks, G.A. 1967. Aqueous surface chemistry of oxides and complex oxide minerals. p. 121-160. *In* W. Stumm (ed.) Equilibrium concepts in natural water systems. American Chemical Society, Washington, DC.

Parks, G.A. and P.L. de Bruyn. 1961. The zero point of charge of oxides. J. Phys. Chem. 66:967-973.

Phillips, I.R. 1999. Copper, lead, cadmium, and zinc sorption by waterlogged and air-dry soil. J. Soil Contam. 8:343-364.

Puls, R.W., R.M. Powell, D. Clark and C.J. Eldrid. 1991. Effects of pH, solid/solution ratio, ionic strength, and organic acids on Pb and Cd sorption on kaolinite. Water Air Soil Pollut. 57-58:423-430.

Purves, D. 1977. Trace-element contamination of the environment. Elsevier, Amsterdam, The Netherlands.

Quantachrome Corporation. 1996. Nova 1200 Gas Sorption Analyzer manual. Quantachrome Corporation, Boyton Beach, FL.

Rhue, R.D., C. Appel and N. Kabengi. 2002. Measuring surface chemical properties of soil using flow calorimetry. Soil Sci. (in press).

Rhue, R.D. and R.S. Mansell. 1988. The effect of pH on sodium-calcium and potassium-calcium exchange selectivity for Cecil soil. Soil Sci. Soc. Am. J. 52:641-647.

Ritchie, G.S.P. and G. Sposito. 1995. Speciation in soils. p. 201-233. *In* A.M. Ure and C.M. Davidson (eds.) Chemical speciation in the environment. Blackie Academic and Professional, Boca Raton, FL.

Rodda, D.P., B.B. Johnson and J.D. Wells. 1996. Modeling the effect of temperature on adsorption of lead(II) and zinc(II) onto goethite at constant pH. J. Colloid Interface Sci. 184:365-377.

Rose, A.W. and G.C. Bianchi-Mosquera. 1993. Adsorption of Cu, Pb, Zn, Co, Ni, and Ag on goethite and hematite: A control on metal mobilization from Red Beds into Stratiform Copper Deposits. Econ. Geol. 88:1226-1236.

Rowlands, W.N., R.W. O'Brien, R.J. Hunter and V. Patrick. 1997. Surface properties of aluminum hydroxide at high salt concentration. J. Colloid Interface Sci. 188:325-335.

Roy, W.R., I.G. Krapac and J.D. Steele. 1993. Sorption of cadmium and lead by clays from municipal incinerator ash water suspensions. J. Environ. Qual. 22:537-543.

Salim, I.A., C.J. Miller and J.L. Howard. 1996. Sorption isotherm-sequential extraction analysis of heavy metal retention in landfill liners. Soil Sci. Soc. Am. J. 60:107-114.

Sanchez, P.A. 1976. Properties and management of soils of the tropics. John Wiley and Sons, Inc., New York, NY.

Santillan-Medrano, J. and J.J. Jurinak. 1975. The chemistry of lead and cadmium in soil: Solid phase formation. Soil Sci. Soc. Am. Proc. 39:851-856.

Sarkar, D., M.E. Essington and K.C. Misra. 1999. Adsorption of mercury(II) by variable charge surfaces of quartz and gibbsite. Soil Sci. Soc. Am. J. 63:1626-1636.

SAS Institute. 1996. Release 6.12. SAS Inst., Cary, NC.

Sauve, S., C.E. Martinez, M. McBride and W. Hendershot. 2000. Adsorption of free lead (Pb^{2+}) by pedogenic oxides, ferrihydrite, and leaf compost. Soil Sci. Soc. Am. J. 64:595-599.

Sauve, S., M.B. McBride and W.H. Hendershot. 1998a. Lead phosphate solubility in water and soil suspensions. Environ. Sci. Technol. 32:388-393.

Sauve, S., M. McBride and W.H. Hendershot. 1998b. Soil solution speciation of lead (II): Effects of organic matter and pH. Soil Sci. Soc. Am. J. 62:618-621.

Scheidegger, A.M., M. Fendorf and D.L. Sparks. 1996. Mechanisms of nickel sorption on pyrophyllite: Macroscopic and microscopic approaches. Soil Sci. Soc. Am. J. 60:1763-1772.

Scheidegger, A.M., D.G. Strawn, G.M. Lamble and D.L. Sparks. 1998. The kinetics of mixed Ni-Al hydroxide formation on clay and aluminum oxide minerals: A time-resolved XAFS study. Geochim. Cosmochim. Acta 62:2233-2245.

Scheinost, A.C., S. Abend, K.I. Pandya and D.L. Sparks. 2001. Kinetic controls on Cu and Pb sorption by ferrihydrite. Environ. Sci. Technol. 35:1090-1096.

Schindler, P.W., P. Liechti and J.C. Westall. 1987. Adsorption of copper, cadmium, and lead from aqueous solution to the kaolinite/water interface. Neth. J. Agric. Sci. 35:219-230.

Schofield, R.K. 1949. Effect of pH on electric charges carried by clay particles. J. Soil Sci. 1:1-8.

Schwertmann, U. and R.M. Taylor. 1989. Iron oxides. p. 379-438. *In* J.B. Dixon and S.B. Weed (eds.) Minerals in soil environments. 2nd ed. Soil Science Society of America, Madison, WI.

Shanableh, A. and A. Kharabsheh. 1996. Stabilization of Cd, Ni and Pb in soil using natural zeolite. J. Hazard. Mater. 45:207-217.

Sloan, J.J., R.H. Dowdy, M.S. Dolan and D.R. Linden. 1997. Long-term effects of biosolids applications on heavy metal bioavailability in agricultural soils. J. Environ. Qual. 26:966-974.

Soil Conservation Service. 1994. Keys to soil taxonomy. 6th ed. United States Department of Agriculture, Washington, DC.

Soil Survey Staff. 1994. Keys to soil taxonomy. 6th ed. SCS, USDA, Washington, DC.

Sparks, D.L. 1999. Kinetics and mechanisms of chemical reactions. p. 135-191. *In* D.L. Sparks (ed.) Soil physical chemistry. 2nd. CRC Press, New York, NY.

Sparks, D.L. and P.M. Jardine. 1981. Thermodynamics of potassium exchange in soil using a kinetics approach. Soil Sci. Soc. Am. J. 45:1094-1099.

Sposito, G. 1981. The operation definition of the zero point of charge in soils. Soil Sci. Soc. Am. J. 45:292-297.

Sposito, G. 1984. The surface chemistry of soils. Oxford University Press, New York, NY.

Sposito, G. 1989. The chemistry of soils. Oxford Univ. Press, New York, NY.

Sposito, G., K.M. Holtzclaw, C. Jouany and L. Charlet. 1983. Cation selectivity in sodium-calcium, sodium-magnesium, and calcium-magnesium exchange on Wyoming bentonite at 298 K. Soil Sci. Soc. Am. J. 47:917-921.

Srivastava, P.C. and U.C. Gupta. 1996. Trace elements in crop production. Science Publ., Inc., Lebanon, NH.

Steinberg, G. 1981. What can you do with surface calorimetry? Chemtech 11:730-737.

Strawn, D.G. 1998. Kinetics and mechanisms of Pb(II) sorption and desorption in soils and soil minerals. Ph.D. Dissertation (Diss. Abstr. AAT 9918894). University of Delaware, Newark.

Strawn, D.G., A.M. Scheidegger and D.L. Sparks. 1998. Kinetics and mechanisms of Pb(II) sorption and desorption at the aluminum oxide water interface. Environ. Sci. Technol. 32:2596-2601.

Strawn, D.G. and D.L. Sparks. 1999. The use of XAFS to distinguish between inner- and outer-sphere lead adsorption complexes on montmorillonite. J. Colloid Interface Sci. 216:257-269.

Strawn, D.G. and D.L. Sparks. 2000. Effects of soil organic matter on the kinetics and mechanisms of Pb(II) sorption and desorption in soil. Soil Sci. Soc. Am. J. 64:144-156.

Su, C.M. and D.L. Suarez. 1997. In situ infrared speciation of absorbed carbonate on aluminum and iron oxide. Clays Clay Miner. 45:814-825.

Tessier, A., P.G.C. Campbell and M. Bisson. 1979. Sequential extraction procedure for the speciation of particulate trace metals. Anal. Chem. 51:844-851.

Thomas, G.W. 1982. Exchangeable cations. p. 159-164. *In* A.L. Page, B.H. Miller and D.R. Keeney (eds.) Methods of soil analysis. 2nd ed. Soil Science Society of America, Inc., Madison, WI.

Thompson, M.L., H. Zhang, M. Kazemi and J.A. Sandor. 1989. Contribution of organic matter to cation exchange capacity and specific surface area of fractionated soil materials. Soil Sci. 148:250-257.

Tiller, K.G., J. Gerth and G. Bruemmer. 1984a. The relative affinities of Cd, Ni, and Zn for different soil clay fractions and goethite. Geoderma 34:17-35.

Tiller, K.G., J. Gerth and G. Bruemmer. 1984b. The sorption of Cd, Zn, and Ni by soil clay fractions: Procedures for partition of bound forms and their interpretation. Geoderma 31:1-16.

Tonner-Navarro, L., N.C. Halmes and S.M. Roberts. 1998. Development of soil cleanup target levels (SCTLs) for Chapter 62-785, F.A.C. Division of Waste Management, Florida Department of Environmental Protection, Gainesville, FL.

Udo, E.J. 1978. Thermodynamics of potassium-calcium and magnesium-calcium exchange reactions on kaolinitic soil clay. Soil Sci. Soc. Am. J. 42:556-560.

Uehara, G. and G.P. Gillman. 1981. The mineralogy, chemistry and physics of tropical soils with variable charge clays. Westview Press, Boulder, CO.

Ulrich, H.J. and C. Degueldre. 1993. The sorption of Pb-210, Bi-210 and Po-210 on montmorillonite – A study with emphasis on reversibility aspects and on the effect of the radioactive decay of adsorbed nuclides. Radiochim. Acta 62:81-90.

Undabeytia, T., S. Nir, G. Rytwo, E. Morillo and C. Maqueda. 1998. Modeling adsorption-desorption processes of Cd on montmorillonite. Clays Clay Min. 46:423-428.

Ure, A.M. and C.M. Davidson. 1995. Introduction to speciation. p. 1-8. *In* A.M. Ure and C.M. Davidson (eds.) Chemical speciation in the environment. Blackie Academic and Professional, New York, NY.

U.S. EPA. 1986. Test methods for evaluation solid wastes: Laboratory manual physical/chemical methods. vol. 1. PB88-239223. U.S. Gov. Print. Office, Washington, D.C.

U.S. EPA. 1991. Remediation of contaminated sediments. EPA/625/6-91/028. U.S. Gov. Print. Office, Washington, D.C.

U.S. EPA. 1992. Common chemicals found at Superfund sites. EPA 540/R-94/044. U.S. Gov. Print. Office, Washington, DC.

U.S. EPA. 1994. National primary drinking water standards. EPA 810-F-94-001A. U.S. Gov. Print. Office, Washington, DC.

U.S. EPA. 1995. Test methods for evaluating solid waste. Vol. IA: Laboratory manual physical/chemical methods, SW 846, 3rd ed. U.S. Gov. Print. Office, Washington, DC.

U.S. EPA. 1996. Soil screening guidance: Technical background document. EPA/540/R-95/128. U.S. Gov. Print. Office, Washington, DC.

van Bladel, R. and H.R. Gheyi. 1980. Thermodynamic study of calcium-sodium and calcium-magnesium exchange in calcareous soils. Soil Sci. Soc. Am. J. 44:938-942.

van Olphen, H. 1977. An introduction to clay colloid chemistry. 2nd ed. John Wiley and Sons, Inc., New York, NY.

van Raij, B. and M. Peech. 1972. Electrochemical properties of some Oxisols and Alfisols of the tropics. Soil Sci. Soc. Am. Proc. 36:587-593.

Weesner, F.J. and W.F. Bleam. 1998. Binding characteristics of Pb2+ on anion-modified and pristine hydrous oxide surfaces studied by electrophoretic mobility and X-ray absorption spectroscopy. J. Colloid Interface Sci. 205:380-389.

Whitting, L.D. and W.R. Allardice. 1986. X-ray diffraction techniques. p. 331-362. *In* A. Klute (ed.) Methods of soil analysis. Part 1. 2nd ed. Agronomy 9. Am. Soc. Agron., Madison, WI.

Wijnja, H. and C.P. Schulthess. 2000. Interaction of carbonate and organic anions with sulfate and selenate adsorption on an aluminum oxide. Soil Sci. Soc. Am. J. 64:898-908.

Wilcke, W., S. Kretzschmar, M. Bundt, G. Saborio and W. Zech. 1998a. Aluminum and heavy metal partitioning in A horizons of soils in Costa Rican coffee plantations. Soil Sci. 163:463-471.

Wilcke, W., J. Mosbach, J. Kobza and W. Zech. 1998b. Distribution of Al and heavy metals in bulk soil and aggregates at three sites contaminated by the emissions of a central Slovak Al smelter. Water Air Soil Pollut. 106:389-402.

Wulfsberg, G. 2000. Inorganic chemistry. University Science Books, Sausalito, CA.

Xia, K., W. Bleam and P.A. Helmke. 1997a. Studies of the nature of binding sites of first row transition elements bound to aquatic and soil humic substances using X-ray absorption spectroscopy. Geochim. Cosmochim. Acta 61:2223-2235.

Xia, K., W. Bleam and P.A. Helmke. 1997b. Studies of the nature of Cu^{2+} and Pb^{2+} binding sites in soil humic substances using X-ray absorption spectroscopy. Geochim. Cosmochim. Acta 61:2211-2221.

Xie, Z. and J.V. Walther. 1992. Incongruent dissolution and surface area of kaolinite. Geochim. Cosmochim. Acta 56:3357-3363.

Yong, R.N. and Y. Phadungchewit. 1993. pH Influence on selectivity and retention of heavy-metals in some clay soils. Can. Geotech. J. 30:821-833.

Yopps, J.A. and D.W. Fuerstenau. 1964. The zero point of charge of alpha-alumina. J. Colloid Sci. 19:61-71.

Zachara, J.M., S.C. Smith, C.T. Resch and C.E. Cowan. 1992. Cadmium sorption to soil separates containing layer silicates and iron and aluminum oxides. Soil Sci. Soc. Am. J. 56:1074-1084.

Zhang, H. 1997. Electrokinetic properties. p. 219-271. *In* T.R. Yu (ed.) Chemistry of variable charge soils. Oxford University Press, New York, NY.

Zhang, M., A.K. Alva, Y.C. Li and D.V. Calvert. 1997. Chemical association of Cu, Zn, Mn, and Pb in selected sandy citrus soils. Soil Sci. 162:181-188.

Zhang, X.N. and A.Z. Zhao. 1997. Surface charge. p. 17-63. *In* T.R. Yu (ed.) Chemistry of variable charge soils. Oxford University Press, New York, NY.

Zhou, Z. and W.D. Gunter. 1992. The nature of surface charge of kaolinite. Clays Clay Miner. 40:365-368.

BIOGRAPHICAL SKETCH

Christopher Stewart Appel was born on October 5, 1970 in Arcadia, California. When he was about 0.5 year old he became Chip Appel courtesy of his older brother Rob who thought Christopher was pronounced Kipper or Chipper whose derivative is Chip. He did his elementary, junior high, and high school work in general education graduating from the finest public schools Laguna Beach, California, had to offer (there was only one of each of these schools). Realizing, much to his chagrin, that due to a gross lack of talent he would not be able to fallow the footsteps of his father into basketball greatness, he became a serious student and began a B.S. in chemistry at California Polytechnic State University, San Luis Obispo. Five years later, he graduated with a degree in biochemistry from the same university in 1995. Sprinkled like seasoning salt amongst his high school and college degrees were two years spent living in France (one year in the middle of high school and another at the end of college). These years did much to shape his life and provided him a still growing desire to work overseas.

In 1996, he began to learn about soil at the same school of his bachelor's degree. He enjoyed this course of study so much that he pursued an M.S. in soil science which was conferred in 1998. Still desiring to learn more about the earth and the media that sustains much of life, he started a Ph.D. program in soil chemistry with Dr. Lena Q. Ma of the University of Florida. Now, December of 2001, he is done but still hungry to learn more about the earth and desirous of applying his knowledge to domestic as well as international tasks.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Lena Q. Ma, Chair
Associate Professor of Soil and Water Science

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Willie G. Harris
Professor of Soil and Water Science

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

R. Dean Rhue
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I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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This dissertation was submitted to the Graduate Faculty of the College of Agricultural and Life Sciences and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

December 2001

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